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THE CHEMISTRY OF SYNTHETIC DYES

VOLUME I

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Diazotization,
Diazonium Salts,
Color, Pyrazolones,
Dyeing, Triazoles.
azo dyes, chemical constitution
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ORGANIC AND BIOLOGICAL CHEMISTRY

—A Series of Monographs—

EDITED BY LOUIS F. FIESER AND MARY FIESER

The Chemistry of
SYNTHETIC DYES

By

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VOLUME I

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Chemistry of syn.

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PREFACE

Chemists interested in dyes have felt for some years the need for a comprehensive survey written from the standpoint of modern organic chemistry. A kind invitation from Professor and Mrs. L. F. Fieser to contribute a volume to a series under their editorship provided the immediate incentive for bringing together notes made during a period of about twenty years as aids to class work and to a program of research in dyes and textile chemistry. The Table of Contents indicates the scope of the present attempt.

Full use has been made of the wealth of information that has now become available on the German dyestuff industry, although it is realized that the processes described in *BIOS*, *CIOS* and *FIAT* reports do not always represent the latest methods actually employed by the Germans; they only serve as a general guide and their authenticity has to be carefully checked both in the laboratory and in works practice. Among the numerous references to books and papers in the body of the book, I am especially indebted to the publications of Fierz-David, Rowe's remarkably extensive account in a hundred pages of the *Development of the Chemistry of Commercial Synthetic Dyes* (two lectures delivered before the Institute of Chemistry, London, in 1938 to mark the Centenary of the birth of Sir William Perkin), the articles on dyes in Thorpe's *Dictionary of Applied Chemistry*, and in particular the excellent reviews on Intermediates and Coloring Matters in the *Annual Reports of the Progress of Applied Chemistry* published by the Society of Chemical Industry, London.

The literature of dyestuff chemistry is largely in patents, but within the limits of this book it has been possible to refer to only a few of them; and with the object of emphasizing recent trends, patent citations mainly cover the last few years. For the older patent literature an essential work of reference is Friedlaender's *Fortschritte der Teerfarbenfabrikation und verwandter Industriezweige*, Vols. I–XXV, Springer, Berlin, 1888–1942. Friedlaender reproduces all the German patents of the years 1877 to 1938 on synthetic dyes (classified broadly according to their chemical constitution) as well as intermediates, pharmaceuticals, plastics and other products derived from coal tar; the corresponding foreign patents are mentioned. The British Patent Office publishes illustrated abridgments of specifications in which dyes are classified as Class 2 (1855–1908), Class 2 (iii) (1909–1930), and Group IV (1931 to date). Section 25 of *Chemical Abstracts* deals with Dyes and Textile Chemistry, and includes abstracts of patents.

PREFACE

It is a pleasure to make grateful acknowledgment of the assistance I have had in writing this book. I am greatly indebted to Professor and Mrs. Fieser for reading several chapters and making many useful suggestions, and to Dr. L. G. S. Brooker for his invaluable criticism of the chapters on Color and Chemical Constitution and Cyanine Dyes. The chapter on Color and its Measurement has been largely written by Dr. B. K. Vaidya. Among others who have read and commented on one or more chapters and to whom my grateful thanks are due are Professor W. Bradley, Dr. S. V. Anantakrishnan, Dr. G. M. Nabar, and Mr. N. R. Kamath. Dr. B. D. Tilak has read the entire book and his suggestions have been very helpful. The irksome task of proof reading has been carried out by Dr. K. H. Shah and Dr. T. B. Panse, to whom I am heavily in debt. I am obliged to Mr. S. B. Dhamankar and Mr. V. D. Ambardekar for typing the manuscript from rough notes.

Much of the work on dyes in my laboratory has been under the auspices of the Council of Scientific and Industrial Research. Without the assistance of Messrs. P. N. Pandit, S. P. Chandavarkar, and P. Jayaraman, and especially of N. R. Rao and B. S. Joshi, Research Fellows working on schemes sponsored by the Council, this book could not have been written. Apart from their work in the laboratory, they have looked up references, entered and checked formulas, prepared the indexes, and helped me in several other ways.

Omissions as well as errors of fact and interpretation are inevitable in dealing with so vast a subject as the chemistry of synthetic dyes and their intermediates, including such topics as the relation between color and constitution, the action of light on dyes, and the affinity of dyes for fibers. I shall be glad to have my attention drawn to errors and to incorporate suggestions for improvement when a revision becomes possible.

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XL. The Action of Light on Dyes and Dyed Fibers
XLI. Chemical Constitution of Dyes in Relation to Substantivity
XLII. Identification, Analysis and Evaluation of Dyestuffs
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Subject Index
Dyestuff Index

Errata:

p. 309, legend to Fig. 2, delete "(Wright)"
p. 312, legend to Fig. 3, delete "(Wright)"
p. 329, legend to Fig. 1, read as
" . . . Absorption of phenol in alcohol (- - - -) . . . . "
p. 373, legend to Fig. 18, line 2, read as
"- - - -, after refluxing in the dark for 45 minutes;"
p. 374, legend to Fig. 19, line 2, read as
"- - - -, on iodine catalysis."

VENKATARAMAN I

List of Abbreviations

Manufacturing companies:

AAP	American Aniline Products Inc., New York
AC	American Cyanamid Co. (Calco Chemical Division), Bound Brook, New Jersey
AGFA	Aktien-Gesellschaft für Anilin-Fabrikation, Berlin
BASF	Badische Anilin- und Soda-Fabrik, Ludwigshafen
BDC	British Dyestuffs Corporation, Huddersfield and Manchester
By	Farbenfabriken vorm. Friedrich Bayer & Co., Leverkusen
C	Leopold Cassella & Co., Frankfurt
CAC	Clayton Aniline Co., Manchester
Ciba (Cb)	Gesellschaft für Chemische Industrie in Basel
DH	Durand und Huguenin A.-G., Basel
DuP	E. I. du Pont de Nemours & Co., Inc., Wilmington, Delaware
GAFC	General Aniline and Film Corporation, New York
GDC	General Dyestuff Corporation, New York
GrE	Chemische Fabrik Griesheim-Elektron, Frankfurt
Gy	J. R. Geigy A.-G., Basel
ICI	Imperial Chemical Industries Ltd., Dyestuffs Group, Grangemouth, Huddersfield and Manchester
IG	Interessen Gemeinschaft für Farbenindustrie A.-G., Frankfurt
K	Kalle & Co., A.-G., Biebrich
Ku	Compagnie Nationale de Matières Colorantes et Manufactures de Produits Chimiques du Nord reunies Etablissements Kuhlmann, Paris
L	Farbwerk Mühlheim vorm. A. Leonhardt & Co., Mühlheim, Frankfurt
LBH	L. B. Holliday & Co. Ltd., Huddersfield
Lev.	Levinstein Ltd., Manchester
MLB	Farbwerke vorm. Meister, Lucius und Brüning, Hoechst
NAC	National Aniline Division, Allied Chemical and Dye Corporation, New York
PhC	Pharma-Chemical Corporation, Bayonne, New Jersey
S	Chemische Fabrik vorm. Sandoz & Co., Basel
SD	Scottish Dyes Ltd., Grangemouth
StD	Société Anonyme des Matières Colorantes et Produits Chimiques de St. Denis, Seine

Journals, Reports and Books:

Except for *JACS* (Journal of the American Chemical Society) and *JCS* (Journal of the Chemical Society, London), the abbreviations of *Chemical Abstracts* for the names of Journals have been followed. The indicated abbreviations have been used for the following.

Annual Repts. Chem. Soc. London	Annual Reports on the Progress of Chemistry, Chemical Society, London
Annual Repts. Soc. Chem. Ind. London	Reports on the Progress of Applied Chemistry, Society of Chemical Industry, London
BIOS	British Intelligence Objectives Sub-Committee Final Report
CI	Rowe, Colour Index, Society of Dyers and Colourists, Bradford, 1924
CIS	*Ibid.* Supplement
CIOS	Combined Intelligence Objectives Sub-Committee Report
FIAT	Field Intelligence Agency Technical Report
OSCV	*Organic Syntheses Collective Volume;* I, 2nd ed., 1941; II, 1st ed., 1943
ST	Schultz, *Farbstofftabellen*, 7th ed., Akademische Verlagsgesellschaft, Leipzig, 1931
ST II	*Ibid.* Zweiter Band, 1932
ST Erg. I	*Ibid.* Ergänzungsband I, 1934
ST Erg. II	*Ibid.* Ergänzungsband II, 1939

Patents:

BeP	Belgian Patent
BP	British Patent
CP	Canadian Patent
DP	Dutch Patent
DRP	German Patent
FP	French Patent
IP	Indian Patent
JP	Japanese Patent
NP	Norwegian Patent

RP	Russian Patent
SP	Swiss Patent
SwP	Swedish Patent
USP	United States Patent

Substituent groups:

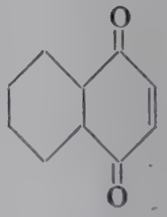
Ac (acetyl); AQ (anthraquinonyl, α or β); Ar (aryl); Et (ethyl); Me (methyl); Ph (phenyl); R (alkyl or aralkyl).

Notes on the Text

Temperatures are in degrees Centigrade.

Double bonds are not shown in benzene, naphthalene, anthracene, pyridine, and other aromatic ring systems. In α-naphthoquinone (I) and anthraquinone (II) the double bonds in the benzene rings are omitted. It is more convenient to represent the phenazthionium cation as (III), instead of (IV). Unless otherwise indicated, rings have been numbered as in Patterson's Ring Index, Reinhold, New York, 1940.

(I)



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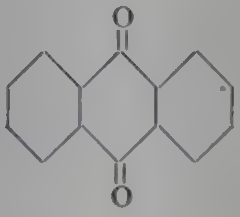

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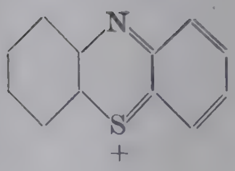
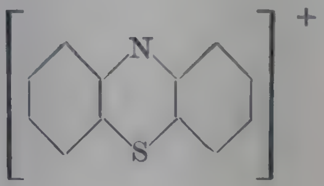


(IV)



The methyl group is numbered 1 for all toluene derivatives including the cresols and the toluidines; xylene derivatives are stated as derivatives of *o*-, *m*- and *p*-xylene; thus 5-chloro-*o*-toluidine is 5-chloro-2-aminotoluene, and *m*-4-xylenol is 2,4-dimethylphenol. Other substituents are numbered in the following order of precedence: carboxyl, hydroxyl, alkoxyl, amino and sulfonic groups. Thus the numbering of salicylic and anthranilic acid derivatives starts from the carboxy group, and of anisidine derivatives from the methoxy group.

CHAPTER 1

INTRODUCTION

In 1771 Woulfe prepared picric acid by the action of nitric acid on indigo, and showed that it dyed silk in bright yellow shades. Laurent in 1842 converted phenol into picric acid, and Perkin in 1856 discovered Mauve, the first synthetic dye to be manufactured and used for practical dyeing. Synthetic organic chemistry was then in its infancy ; as late as 1847 Berzelius was writing in support of the belief that a " vital force " was necessary for the production of organic compounds. Faraday discovered benzene in 1825 and Hofmann isolated it from coal tar in 1845; but the chemistry of benzene and its derivatives had made no real beginning at the time of Perkin's synthesis of Mauve, since it preceded by nearly a decade Kekulé's concept of the structure of benzene. With the simultaneous and largely interdependent progress made during the last ninety years in dyestuff chemistry and in organic chemistry, synthetic dyes have been prepared in bewildering number and variety, and the possibilities of further synthesis are unlimited. Dyes which appear at first to be of practical interest are submitted to a careful appraisal in the laboratories of dyestuff manufacturers, and those which have found a permanent place in commerce represent the survival of the fittest. For every dye used commercially, there are perhaps a hundred which have proved valueless for one reason or another ; at least 1,500 dyes are at present employed by the textile and other color-using industries, so that the scale on which research on synthetic dyes has been proceeding can be readily imagined. The Color Index (1924) describes 1,230 dyes ; the number of commercial dyes has increased in the intervening period, but a more important change is that many of the dyes mentioned in the Color Index are obsolete, while new dyes with improved properties have been marketed.

Simultaneously with developments in the dyestuff industry, and indeed as a direct result, there has been continual progress in the chemical technology of textiles. It is obviously in the interests of dyestuff manufacturers to maintain laboratories which provide information and technical service concerning the application of their products, but they have gone far beyond the limits of user requirements and have been responsible for many new processes in dyeing, printing and finishing textiles, particularly the new fibers, some of which (e.g., nylon) have been discovered and are manufactured by dyestuff organizations.

Until recently coal tar was the sole raw material for the synthetic dyes, and an important effect of their commercial development has therefore been the isolation and study of an increasing number of coal-tar constituents. The chemistry of a series of carbocyclic and heterocyclic compounds was thus actively pursued. The synthesis of a dye from a coal-tar constituent involves a large number of intermediate compounds and reactions, and these in their turn have led to numerous advances in organic chemistry and the organic chemical industries. Color chemistry has also stimulated quantum-mechanical studies of the relation between light absorption and the electronic structure of simple and complex molecules. The dominant position occupied by Germany in the dyestuff industry before the first world war was largely due to the encouragement of research in the chemistry of dyes and in organic chemistry as a whole. After 1916 Great Britain and the United States took vigorous measures for the consolidation and development of their dyestuff industries. British and American dyestuff firms sponsored extensive programs of research in their own laboratories and in the universities, covering not merely the requirements of the industry, but also fundamental problems of color, fiber structure, the affinity of dyes for fibers, chemotherapy, and numerous other aspects of organic and biological chemistry.

HISTORY OF THE SYNTHETIC DYES[1-3]

In the course of attempts[4] to synthesize quinine by the addition of oxygen to allyltoluidine, Perkin studied the action of potassium dichromate on aniline sulfate, and from the very unpromising-looking black product, he isolated in 1856 a small amount of a mauve coloring matter which dyed silk directly. He had the vision to foresee immediately the tremendous industrial importance of his observation, and overcoming all the obstacles that stood in his way he built in June 1857 a factory for the manufacture of Tyrian Purple (Aniline Purple; Mauve; Mauveine). Perkin's essential achievements were the translation of a casual laboratory observation into manufacturing practice and his success in demonstrating the value of his product to the dyer and printer. Runge had noticed in 1834 the formation of rosolic acid (aurine) when phenol was oxidized, but a practicable process was not worked out till 1861 (Kolbe and Schmitt). Similarly Perkin established the large-scale production of nitrobenzene and aniline, while

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[1] Caro, Uber die Entwickelung der Teerfarben-Industrie, Deutsche chemische Gesellschaft, Berlin, 1893.

[2] Rowe, The Development of the Chemistry of Commercial Synthetic Dyes (1856-1938). Institute of Chemistry, London, 1938.

[3] Rowe, *J. Soc. Dyers Colourists* **54**, 551 (1938).

[4] Sir William Perkin, Hofmann Memorial Lecture, *JCS* **69**, 603 (1896).

nitrobenzene had been made earlier by Mansfield (1847) and aniline by Hofmann. Mauve was applicable to silk and wool, but not to cotton, and Perkin thereupon developed a process for dyeing cotton after mordanting it with tannin and sodium stannate. Brilliant shades were thus obtained, and this notable addition to dyeing technique, which continues to be used to the present day with the modification that tartar emetic has replaced the tin salt, led to the synthesis and use of other basic dyes. Magenta was made by the French chemist Verguin in 1859 by heating crude aniline with stannic chloride; arsenic acid (Medlock, Nicholson, 1860) and ultimately nitrobenzene (Coupier, 1868) were used for this oxidation. The preparation of derivatives of Magenta followed soon after. *N*-Phenylation gave Aniline Blue and Imperial Violet (Girard and de Laire, 1860) and subsequent sulfonation gave the acid dyes, Soluble Blue and Alkali Blue (Nicholson, 1862). Lauth (1861) prepared Aldehyde Blue by heating Magenta with sulfuric acid and acetaldehyde, and Cherpin (1862) prepared the first green dye, Aldehyde Green, by the treatment of Aldehyde Blue with sodium thiosulfate. Nicholson (1862) isolated the first acridine dye, Phosphine, by working up Magenta residues. Methylation of Magenta yielded the Hofmann Violets (1863) and Iodine Green (Keisser, 1866). Perkin prepared Safranine in 1863 by the oxidation of Mauve with lead peroxide. In 1866 Bardy oxidized a mixture of mono- and dimethylanilines to Methyl Violet, which soon eliminated the Hofmann Violets. In the same year as Perkin's Mauve, Greville Williams discovered Cyanine (or Quinoline) Blue, which was valueless as a dye on account of the very poor fastness of the shades; but the Williams reaction of condensing alkyl halides of quinoline and lepidine led, half a century later, to the synthesis of a whole series of photographic sensitizers.

Griess discovered diazotization in 1858, and the coupling of diazonium salts in 1864. Aminoazobenzene had been made a little earlier and converted into Induline (Dale and Caro, 1863), and Bismarck Brown was also made in 1863 by Martius by the action of nitrous acid on *m*-phenylenediamine; but the reactions involved were not understood at the time.

Lightfoot in 1863 discovered the first ingrain dye or dye produced on the fiber, when he impregnated cotton with aniline and then oxidized it to Aniline Black. The chemistry of the coloring matter and the mechanism of the reactions that took place were not explained till half a century later (Willstätter, A. G. Green, 1913).

The Badische Anilin und Soda Fabrik (BASF) commenced dye manufacture at Ludwigshafen in 1863, and for some sixty years thereafter Germany led the world in the chemistry and technology of dyes. When Germany commenced dyestuff manufacture, she was mainly dependent on England for the supply of coal tar, but the recovery of tar from existing coke ovens was then undertaken and new by-product coking plants were also installed. Graebe and Liebermann in 1868 achieved the first synthesis of a natural coloring matter by converting dibromoanthraquinone into Alizarin; on two successive dates in 1869 Caro, Graebe and Liebermann in Germany and Perkin in England patented a process for Alizarin in which sulfonated anthraquinone was fused with caustic alkali. The formation of phenols by the alkali fusion of the alkali salts of aromatic sulfonic acids was observed in 1867 (Kekulé, Wurtz), and resorcinol was manufactured soon after. In 1871 a series of phthalein dyes were made: Fluorescein, Gallein and Cerulein (Baeyer), Eosine (Caro). Kekulé's brilliant intuition regarding the structure of benzene led to a systematic study of the constitution of the aromatic hydrocarbons and their derivatives. In 1870 Kekulé coupled diazotized aniline with phenol, and in addition to making the first hydroxyazo dye he determined the constitution of the azo compounds. The simplicity and versatility of the diazotization and coupling reactions resulted in the preparation of a large number of azo dyes, which still remain the most numerous group among the coloring matters. In 1875 Caro made Chrysoidine; and in 1876 Roussin made Orange II and IV, and Griess other azo dyes from diazotized sulfanilic acid. Fast Yellow (Koehler, 1877), the Ponceaus (Baum, 1878), the disazo dye Biebrich Scarlet (Nietzki, 1879), and Metanil Yellow (1880) are examples of other azo dyes made during this period. Further important discoveries during 1876-1879 included the thiazine dye Methylene Blue (Caro, 1876), which has remained one of the most important basic colors; Alizarin Orange or 3-nitroalizarin (Rosenstiehl, 1876); Alizarin Blue (Prud'homme, 1877) which is a pyridine derivative of Alizarin and led to the Skraup synthesis of quinoline; Malachite Green (O. Fischer, 1877), a still valuable basic dye of the triphenylmethane group; and the first oxazine dye, Meldola's Blue (1879). While acid dyes of the triphenylmethane series can be prepared by sulfonating the basic dyes containing amino or alkylamino groups, sulfonation is much more facile if an *N*-benzyl group is present (Koehler, 1879), or alternatively, the triphenylmethane condensation can be carried out with benzylethylanilinesulfonic acid; and these and similar methods have since been used for making a series of violet, blue, and green acid dyes for wool.

The year 1880 was notable for two events. Baeyer synthesized indigo; and Read, Holliday and Sons developed the Para Red process, in which an insoluble azo dye is produced by impregnating cotton with alkaline β-naphthol and then coupling with diazotized *p*-nitroaniline. In 1883 Kern used phosgene for the preparation of a triphenylmethane dye, Crystal Violet; and he prepared Auramine by fusing 4,4′-bis-dimethylaminobenzophenone with ammonium and zinc chlorides. In the same year (1883) Walter made Sun Yellow, the first stilbene dye and the first soluble dye which dyed cotton without the aid of a mordant; but the chemistry of the complex reactions which took place when 4-nitrotoluene-2-sulfonic acid was treated with alkali was not elucidated until 1897-1908 (Green and Wahl), during which period were made a series of useful yellow, orange and brown azo and azoxy dyes derived from stilbene (e.g., Mikado Orange and some of the Diphenyl Fast colors). Congo Red, the first direct cotton dye from benzidine, was discovered by Boettiger in 1884. In spite of its fugitive character Congo Red continues to be made at the present day on an enormous scale, and hundreds of other direct cotton colors have been synthesized by coupling tetrazotized benzidine and analogous diamines with various components. The first azo dye of the pyrazolone series, Tartrazine, was also made in 1884 (Ziegler) by two methods, one of which, the condensation of a phenylhydrazine derivative with a β-ketonic ester, constituted a valuable general reaction for pyrazolone synthesis. Although the first sulfur dye, Cachou de Laval, was made by Croissant and Bretonnière in 1873 by heating carbohydrate wastes with alkali and sulfur, the first thionation process leading to a dye of definite constitution was carried out by Green in 1887 when he prepared Primuline Base by heating *p*-toluidine with sulfur. Sulfonation gave Primuline which was a yellow direct cotton dye, valueless as such, but used for many years for the production of relatively fast shades by diazotizing on the fiber and developing (i.e., coupling the diazonium salt) with β-naphthol, resorcinol, *m*-phenylenediamine and other components. The Bohn-Schmidt reaction for the preparation of polyhydroxyanthraquinones by the action of oleum on alizarin and other anthraquinone derivatives, which is widely applicable for the synthesis of anthraquinonoid intermediates and dyes, was discovered in 1888. Important azo chrome colors for wool, such as Diamond Black F and the Chromotropes, were made in 1889-90 (Lauch, Krekeler, Kuzel); and Naphthol Blue Black (M. Hoffmann), a disazo dye from H-acid and the most widely used black dye for wool, was made in 1891. Graebe and Liebermann had found in 1871 that Alizarin could be sulfonated to give a soluble wool dye, and during the period 1893-97 Schmidt made a series of valuable blue and green dyes for wool (e.g., Alizarin Saphirol and Alizarin Cyanine Green), derived from the aminoanthraquinones and the aminohydroxyanthraquinones. The Alizarin Sky Blue type (Unger, 1899) is made by condensing 2,4-dibromo-l-aminoanthraquinone with an arylamine, followed by sulfonation. The period 1893-99 is also notable for the discovery of the process of thionation by means of sodium polysulfide solution, and of the Sulfur Blacks—Vidal Black, Immedial Black FF (Kalischer), and Sulfur Black T (Priebs and Kaltwasser); the last, prepared by the thionation of 2,4-dinitrophenol, remains today among the three or four of the bulkiest products of the dyestuff industry.

Baeyer's synthesis of indigotin in 1880 was of great scientific interest, but it was only in 1890 that Heumann developed a technical synthesis in which phenylglycine or its *o*-carboxylic acid was fused with caustic potash, and it took a further seven years for the actual industrial production of indigo. Phenylglycine-*o*-carboxylic acid, made from anthranilic acid, gave a much better yield, and since phthalic anhydride was a necessary intermediate in this process, the oxidation of naphthalene to phthalic anhydride was closely investigated. The accidental breakage of a thermometer led to the use of mercury as a catalyst for oxidizing naphthalene with fuming sulfuric acid (Sapper, 1896). In 1899 Sandmeyer worked out a synthesis of indigotin from aniline via isatin-α-anilide, which was inferior to the Heumann process, but proved useful for the manufacture of other indigoid and thioindigoid dyes. Roessler showed in 1902 that indigotin could be obtained in equally good yield from phenylglycine or its *o*-carboxylic acid if sodamide is used in the fusion.

The present century opened with the outstandingly important discovery of Indanthrene Blue (Bohn, 1901), a product of the alkali fusion of β-aminoanthraquinone. The next few years saw the synthesis of a series of anthraquinone vat dyes, of which examples are Indanthrene Yellow G or Flavanthrone (Bohn, 1901), Indanthrene Dark Blue BO or dibenzanthrone, Green B and Black BB (Bally and Isler, 1904), Indanthrene Golden Orange G (Scholl, 1905), the di- and trianthrimides such as Algol Orange R and Indanthrene Red G (Isler, 1905-1907), Indanthrene Violet R or isodibenzanthrone (Bally, Wolff, 1906), Algol Yellow R (Indanthrene Yellow GK) or 1,5-dibenzamidoanthraquinone (Noelting and Wortmann, 1906), Algol Brilliant Violet R (Indanthrene Brilliant Violet RK) or 1,5-dihydroxy-4-8-dianisoylamidoanthraquinone (Thomaschewski, 1908), the anthraquinonecarbazoles such as Indanthrene Brown GR, Olive R and Khaki GG (Uhlenhuth, Mieg, MLB, 1908-1911), and the anthraquinone-acridones such as Indanthrene Violet RN, Red BN and Red Violet RRN (Ullmann, Bally, Lüttringhaus, 1909-1910). These dyes are especially suitable for dyeing cotton and the regenerated cellulose fibers, and the shades in general possess excellent fastness. It is often not realized that, notwithstanding the discovery and large-scale production of several artificial and synthetic fibers, cotton continues to be preeminent as a fiber and is used in over 70% of all textiles. Since fast dyes for cotton were till then unknown, the discovery of the anthraquinonoid vat dyes was of very great commercial importance. On the scientific side, Indanthrene Blue stimulated intensive research on anthraquinone chemistry, which has resulted in the synthesis of a large number of complex ring systems of both carbocyclic and heterocyclic types, involving novel condensations and new methods of cyclization such as the Scholl reaction using aluminum chloride. Bohn noticed (1903) that Indanthrene

Blue could be halogenated in sulfuric acid, and methods of halogenation by sulfuryl chloride and antimony pentachloride and in solvents such as nitrobenzene have since been evolved ; these were applied with particular success in producing faster dyes in the indigoid and thioindigoid series (Engi, 1907), Thioindigo having been synthesized by Friedländer in 1906.

During this period (1900-1910), there were also advances in other directions. The first blue sulfur dye (Immedial Pure Blue) was made in 1900 (Weinberg and Herz), and a green dye (Pyrogene Green) in 1904 (Boeniger), by heating certain indophenols with aqueous sodium polysulfide. Direct cotton dyes derived from J-acid (e.g., Benzo Fast Scarlet 4BS and the Rosanthrenes) were made (Israel and Kolthe, Bertschmann, 1900-1902). Cyanine dyes (e.g., Ethyl Red, Pinaverdol, Pinacyanol) were marketed as color sensitizers for photography (Miethe and Franke, Koenig, 1903-1905). Hydron Blue R (Haas, 1908), prepared by the thionation of carbazole-indophenol, was the first representative of the class of sulfurized vat dyes, and it is largely used for dyeing navy blue shades on cotton. The sulfurization of anthraquinone derivatives (e.g., 2-methylanthraquinone and 4-methylbenzanthrone) to give vat dyes (e.g. Cibanone Yellow R, Orange R and Blue 3G) was carried out almost simultaneously (Mayer, Pfannenstiehl and Schaarschmidt).

In 1911 Indanthrene Khaki GG (MLB), a carbazole from pentanthrimide, was marketed, and this fast vat dye was produced in large quantities during the second world war. The year 1912 is notable for the introduction of Naphtol AS by Griesheim-Elektron; this compound, the anilide of 2-hydroxy-3-naphthoic acid, was made by Schöpff in 1892, but its advantages over β-naphthol as a coupling component in the Para Red method of dyeing and printing were not noticed. The azoic dyes produced from Naphtol AS and its analogs, which now provide a full range of brilliant and fast shades from yellow to black, constitute a group second in importance only to the anthraquinonoid vat dyes for application to the cellulose fibers. Brilliant lakes for paints and varnishes have long been made from triphenylmethane dyes by precipitation of the basic dyes with tannin-antimony and the acid dyes with barium salts, but they had poor fastness to light, and a valuable observation made in 1913 by the BASF was that the phosphotungstic acid and phosphomolybdic acid lakes are much faster. Another discovery (Herzberg) in 1913 was the Alizarin Direct Blue A type of acid dye, made by the condensation of 4-bromo-1-aminoanthraquinone-2-sulfonic acid with arylamines.

The war of 1914-1918 created a gap in the progress of dyestuff chemistry, and the next stage is covered by the period 1920-1938. However, two developments of considerable interest occurred during the war years.

Following the work of Bohn and the BASF in 1912 on the Ergan dyes, which were chromium complexes of azosalicylic acids useful for calico printing, the Society of Chemical Industry in Basle marketed the first Neolan dye in 1915; the Neolans, of which there are now over forty, are preformed water-soluble chromium complexes of mordant azo dyes, which are applicable to wool and silk directly and eliminate the need for the dyer to carry out a mordanting process. The second discovery, which has had a profound influence on the dyestuff and related industries, was the air oxidation of naphthalene to phthalic anhydride in the vapor phase using vanadium pentoxide as catalyst (Gibbs, 1917). The very low price at which phthalic anhydride thus became available not only lowered the cost of dyes such as indigo, but also made it possible to use the phthalic anhydride route to anthraquinone and its derivatives. As a result, fast dyes of the anthraquinone series were made cheaper and the range was continually expanded.

A very important discovery made soon after the war was the methylation of dihydroxydibenzanthrone to the dimethyl ether, Caledon Jade Green (Davies, Fraser-Thomson and Thomas, 1920); this fast and brilliant dye filled a gap in the color range of the anthraquinonoid vat dyes. Indanthrene Golden Yellow GK, the first vat dye of the dibenzpyrenequinone class, was made in 1922 (Kranzlein, Corell and Sedlmayr). While the yellow vat dye anthanthrone (Kalb, 1913) had no practical value, it was found in 1925 (Herz and Zerweck) that halogenation gave fast and brilliant vat dyes (Indanthrene Brilliant Orange GK and RK). In 1924-1926, vat dyes derived from naphthalene- and perylene-peri-tetracarboxylic acids were marketed, e.g., Indanthrene Red GG and Scarlet GG (Eckert and Greune). After 1920 new members of the Naphtol AS series were continually added, simultaneously with suitable bases (Fast Bases) for diazotization and coupling. Naphtol AS-G (*bis*-acetoacet-*o*-tolidide) for the production of yellow shades was marketed in 1921 (Laska and Zitscher). Among the more recent Fast Bases, some have the interesting feature of a trifluoromethyl group, and the IG have made an extensive study of fluorine compounds. Nitrosamine Red (sodium *p*-nitrophenyl *anti*-diazotate) was marketed as a stabilized diazo compound for use in dyeing and printing as early as 1893, and mixtures of a series of such *anti*-diazotates with Naphtols were marketed during 1920-1930 as Rapid Fast colors for printing. Diazonium salts, stabilized in various forms, were also introduced. With the preparation of the first Indigosol (DH) by Bader and Sunder in 1921, vat dyes became available in a water-soluble form as the sulfuric esters of the leuco derivatives, so that the stage of vatting could be eliminated. Using an improved one-stage method of reduction and sulfation (Harris *et al*; 1924), the Soledons (ICI) were then marketed. Hydrolysis and oxidation on the fiber are necessary for the development of the Indigosols and Soledons, and for this and other reasons, of which the cost is one, they are still of much more limited use than the parent vat colors in cotton dyeing. In calico printing, they are invaluable, as they provide the only convenient method by which vat reserves under a vat ground can be obtained. The cyanine dyes, including several new types, were intensively studied from 1920 onwards, especially by the Eastman Kodak Co. In 1922 König found that some of the cyanines are useful for dyeing and printing cotton, and an example is Astraphloxine FF (IG). Cellulose acetate rayon, differing sharply from cotton and viscose in its affinity for dyes, had long presented serious dyeing problems, and the Ionamines (Green and Saunders, 1922), formaldehyde-bisulfite condensates of insoluble aminoazo compounds, were the first important dyes for this fiber. Almost immediately thereafter it was found (Baddiley and Shepherdson; Ellis, 1923) that cellulose acetate can be readily dyed in fast shades by aqueous dispersions of insoluble azo dyes as well as anthraquinone derivatives. Chlorantine Fast Green BLL (Ciba, 1924) is a direct cotton dye with good fastness to light, its synthesis involving the interesting principle of combining blue and yellow azo dye units by condensation with cyanuric chloride. Blue direct cotton dyes of unusual fastness to light have been made by condensing chloranil with compounds such as 3-amino-*N*-ethylcarbazole to form oxazines (Kranzlein, Greune and Thiele, 1928). Vat dyes of the anthraquinone-acridone class have received fresh attention since 1928, when Indanthrene Turquoise Blue GK and 3GK (Berliner) were marketed. The Rapid Fast range of azoic printing colors was supplemented in 1930 by the Rapidogen colors (IG), in which the diazonium component is stabilized by condensation with amino acids; and it is likely that the Rapidogens will ultimately replace the earlier type. Two useful vat dyes were marketed in 1931: Indanthrene Brilliant Orange GR, a component of Indanthrene Scarlet GG mentioned earlier which is a mixture of two stereoisomeric dyes; and Indanthrene Navy Blue R (Wilke) which is a derivative of pyrazolanthrone. The Carbolan dyes (ICI, 1933) are acid azo or anthraquinone dyes, mostly the latter, some containing heavy alkyl groups attached to nitrogen or oxygen, and characterized by excellent fastness to wet treatments. An event of great interest in the chemistry and technology of dyes was the manufacture of copper phthalocyanine, Monastral Fast Blue BS (ICI), in 1934. The formation of a blue pigment during the manufacture of phthalimide in an iron pan was noticed by Dandridge in 1928, and the chemistry of the phthalocyanines, which are synthetic analogs of chlorophyll and hemin, was elucidated by Linstead. While copper phthalocyanine and its pentadecachloro derivative are brilliant blue and green pigments of unusual stability, their only disadvantage being the cost in comparison with inorganic pigments, phthalocyanine derivatives have been more recently prepared which are useful for dyeing and printing textiles. Examples are Sirius Light Turquoise Blue GL (IG) and Alcian Blue 8G (ICI, 1947). During 1934-1937 the IG added several new members to their anthraquinonoid vat dye range. The Solacet Dyes (ICI, 1936) are soluble azo and anthraquinone dyes for acetate silk, the device of sulfating an N-β-hydroxyethyl group being used for solubilization without prejudice to the affinity for the cellulose ester.

INDUSTRIAL ORGANIZATION

Having originated in England with the firm of Perkin and Sons, the dyestuff industry progressed rapidly in Germany after the establishment of the Badische Anilin und Soda Fabrik (BASF) at Ludwigshafen in 1865, followed during the next few years by Farbwerke vormals Meister, Lucius and Brüning (MLB) at Höchst, Farbenfabriken Bayer at Elberfeld, Aktiengesellschaft für Anilinfabrikation (AGFA) at Berlin, Leopold Cassella at Frankfurt, Kalle and Co. at Biebrich am Rhein, Chemische Fabrik Griesheim-Elektron at Griesheim, and a number of smaller factories. In 1904 AGFA merged in BASF, and an agreement was also entered into with Bayer for the division of markets and exchange of patents. Simultaneously MLB purchased the controlling interest in Kalle and Cassella. Faced for the first time with serious competition from other countries the six large dyestuff firms in Germany (BASF, MLB, Bayer, Cassella, Kalle and Griesheim-Elektron) amalgamated themselves in 1924 into a combine, the Interessen Gemeinschaft für Farbenindustrie A.G. (IG), which controlled over 60% of the capital of the entire German chemical industry. Following Germany's defeat in the second world war, the great German color trust, which had helped the Nazi party in its rise to power, was broken up into its component units.

Switzerland has had for many years a highly developed dyestuff industry which specializes in the more expensive dyes and has to its credit several contributions to dyestuff chemistry. Over 95% of Swiss production is exported. There are four manufacturing firms: Ciba (formerly the Society of Chemical Industry in Basle), Geigy, Sandoz, and Durand and Huguenin, the last having been associated with the IG until 1939. After the first world war Ciba, Sandoz and Geigy organized themselves into the Basler Interessen Gemeinschaft (Swiss IG). While the Swiss industry is strong in the manufacture of finished dyes, it depends largely on Germany in normal times for coal-tar primaries as well as the bulk intermediates.

The outbreak of war in 1914 brought home to many countries, particularly to the United States and Great Britain, the full significance of German domination in the dyestuff industry and its very close connection with organic chemicals in general, including explosives, synthetic drugs, and rubber chemicals.[5-8] With a large subsidy from the British Government, a new company (British Dyes Ltd.) was formed in 1915, which absorbed the long established firm of Read Holliday and Sons of Huddersfield. In 1919 the British Dyestuffs Corporation was formed by the merger of British Dyes with Levinsteins of Manchester, another of the old British firms (founded in 1864) that had withstood German competition. The factory of Claus and Co. at Clayton and the synthetic indigo plant of MLB at Ellesmere Port were also taken over. In the same year the import of dyes and intermediates, unless specially licensed by the Board of Trade in the interests of the dye-consuming industries, was prohibited by an Order in Council. Since the Order could not be enforced in view of an adverse legal decision, the Dyestuffs (Import Regulation) Act was passed in 1920, and is still in force. In 1926 Imperial Chemical Industries was formed by the amalgamation of Brunner Mond and Co., Ltd., Nobel Industries Ltd., United Alkali Co., Ltd., and British Dyestuffs Corporation Ltd.; Scottish Dyes, formerly Solway Dyes, also became part of ICI at the same time. The British Alizarin Co. joined ICI in 1931. Several other companies (e.g., British Copper Manufacturers and Mond Nickel Co.) having also been acquired a little earlier, ICI ultimately constituted a consolidation of interests in dyes, heavy chemicals, explosives, pharmaceuticals, plastics, paints, rayon, synthetic gasoline, metals, and in fact the whole field of chemical industry.[9] In 1946 ICI, which had a consolidated balance sheet of over £140,000,000 and whose activities were industrially and geographically all-embracing, announced a £9,000,000 expansion project allocated to dyes, synthetic drugs and plastics.[10] The British production of dyes in 1938 met over 90% of domestic requirements. Outside ICI there are a few dye-manufacturing firms in Great Britain of which the largest are L. B. Holliday and Co., of Huddersfield, the Clayton Aniline Co., of Manchester, which is owned by the Swiss group, and J. W. Leitch and Co., of Huddersfield.

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[5] Report of the Dyestuff Industry Development Committee of the Board of Trade, London, 1930, 1932.

[6] Morgan and Pratt, British Chemical Industry, Arnold, London, 1938.

[7] Haynes, American Chemical Industry, Vols. I-IV, Van Nostrand, New York, 1945-48.

[8] Dyes, War Changes in Industry Series Report No. 19, U.S. Govt. Printing Office, Washington, 1946.

[9] Levy, Monopolies, Cartels and Trusts in British Industry, Macmillan, 1927.

[10] *Financial Times*, London, May 4, 1946.

In 1914 the United States[7, 8] produced less than 3% of the world output of dyes and about 10% of the country's consumption, which was more than that of any other country. There were seven small dyestuff factories in 1915, of which the largest was the Schollkopf Aniline and Chemical Co. of Buffalo, but by the beginning of 1918 over seventy new factories had come into existence. The U.S. Government seized German-owned plants and made the German-owned patents filed in the United States available to the domestic dye industry. In 1918 the import of dyestuffs from enemy countries was prohibited; and the Dye and Chemical Control Act of 1921 prohibited the import of all dyes and coal-tar derivatives unless these were "not reasonably obtainable from domestic industry." The production in 1923 was 93,667,524 pounds, which represented about 95% of domestic consumption and included a substantial export trade. In 1938 the United States was second only to Germany in dyestuff production. The 1946 production was 186 million pounds and the 1947 production 212 million pounds.[11] Forty American dyemakers are listed in the Handbook of the AATCC, and among them may be mentioned the National Aniline and Chemical Co. (a component firm of Allied Chemical and Dye Corporation), du Pont de Nemours and Co., the Calco Chemical Division of the American Cyanamid Co., General Aniline and Film Corporation (GAFC), Ciba, Geigy, and Sandoz. The last three are American counterparts of the Swiss firms ; besides selling Swiss-made dyes, they operate the Cincinnati Chemical Works to supplement the Swiss range of dyes. Ciba also sell the dyes of the Dow Chemical Co. The General Dyestuff Corporation (GDC) was formed in 1925 by a merger of Metz, sales agency for MLB, and of the manufacturing firms of the Consolidated Color and Chemical Co., and the Central Dyestuff and Chemical Co. The sales agencies for Cassella, Bayer, and BASF dyes were also obtained. In 1929 the IG bought the Grasselli Dyestuff Corporation, renaming it the General Aniline Works, and organized the American IG Chemical Corporation. In 1939 all the IG interests were consolidated into GAFC, which became one of the large producers of dyestuffs and miscellaneous organic chemicals and the sole agent for all IG products in the United States. A corporation set up by the United States Alien Property Custodian has been operating the GAFC plants since 1942. At the present time GDC has the selling agency for General Aniline Works, a division of GAFC and for Marietta Dyestuff Co.

[7, 8] See p. 11.

[11] U.S. Tariff Commission Report, quoted in *Chem. Eng. News*, **26**, 2943 (1948).

Over 60% of the total United States output of dyes is produced by three firms: du Pont, NAC and Calco; and about 20% by GAFC and Cincinnati Chemical Works.

In France Renaud Brothers and Franc commenced dyestuff production at Lyons almost immediately after the industry was founded in England, but soon lost ground to the German factories. There were only two French-owned dyestuff factories in 1914: St. Denis (formerly Poirrier) and Etablissements Steiner; and the combined production was less than 10% of the domestic consumption. The Societé Anonyme des Matieres Colorantes de St. Denis and the Compagnie Nationale des Matiere Colorantes were created during the first world war under government auspices; and the two, together with smaller firms, merged into the Etablissements Kuhlmann in 1926. During the German occupation of France all the French dyestuff groups were amalgamated into a single organization, Francolor, under the control of the IG. After the liberation of France the French Government decided to maintain the unity of Francolor in the interest of a strong French dyestuff industry. The shares held by the IG became the property of the French Government. The total productive capacity of the French factories is about 20,000 tons.

In Italy Montecatini is the leading chemical corporation and is associated with the IG, especially for dyestuffs. There is a state-controlled dyestuff industry in Russia, and there are state-aided factories in Japan. Nearly two-thirds of the Japanese production of 37,200 tons of dyes in 1939 consisted of sulfur dyes. In 1938 the main dye-manufacturing countries were Germany, the United States, Russia, Japan, Great Britain, Italy, Switzerland and France. From 1927 until the outbreak of war in 1939, IG, ICI, Kuhlmann, and the Swiss firms had commercial agreements, so that the dyestuff and allied chemical industries have had international ramifications. Table I gives the production, exports and imports of eight countries in 1938. Tables II and III give the quantities and the value in dollars of the major dyes and intermediates produced in the United States. The position of the dyestuff industry in 1946 has been surveyed in "World chemical developments 1940-46," published by the United States Department of Commerce. The United States has now become the world's largest producer and exporter of coal-tar dyes. The United Kingdom production of dyes in 1946 was hampered by the shortage of coal, but nevertheless totalled about 67 million pounds (50% more than the 1938 production), valued at £12,000,000. France produced 12,000 metric tons in 1946 and in 1938. The Swiss export of dyes in 1946 amounted to about 16 million pounds valued at 175,776,000 francs.

TABLE I[8]

COAL-TAR COLORS, DYES AND STAINS : PRODUCTION, EXPORTS AND IMPORTS BY PRINCIPAL PRODUCING COUNTRIES, 1938

Country	*Production*	*Exports*			*Unit value*	*Imports*		
		Quantity	*Value*			*Quantity*	*Value*	*Unit value*
			Total	*Per cent of total*				
	Million pounds	*Million pounds*	*Million dollars*		*$ per pound*	*Million pounds*	*Million dollars*	*$ per pound*
Germany ..	135.0	60.6	43.8	52.4	0.72	6.2	5.0	0.81
United States ..	81.8	8.6	3.8	4.6	0.45	3.3	5.1	1.53
Soviet Union ..	77.8	0.3	0.1	0.1	0.20	0.4	1.1	3.10
Japan	63.2	18.6	2.7	3.2	0.14	0.6	0.8	1.45
United Kingdom	45.5	8.9	5.5	6.6	0.62	4.8	6.7	1.40
Italy	23.5	2.3	0.8	1.0	0.35	0.8	1.6	1.97
Switzerland ..	16.2	14.6	19.0	22.7	1.29	1.5	1.8	1.22
France	20.0	9.5	5.1	6.0	0.53	2.7	4.1	1.52

TABLE II[12], [13]

QUANTITIES AND VALUE OF SOME COAL-TAR DYES PRODUCED IN THE UNITED STATES IN 1941 AND 1945

Dye	1941		1945	
	Production 1000 *pounds*	*Unit value, $ per pound*	*Production* 1000 *pounds*	*Unit value, $ per pound*
Orange II	1,582	0.28	1,366	0.27
Chrome Blue Black R ..	1,944	0.27	1,593	0.29
Acid Black 10B	1,583	0.39	1,431	0.40
Direct Fast Scarlet	1,129	1.02	990	1.04
Bismarck Brown G ..	149	0.36	86	0.38
Bismarck Brown R ..	974	0.40	839	0.43
Developed Black BH ..	3,217	0.32	2,531	0.33
Direct Blue 2B	1,548	0.21	994	0.23
Benzopurpurine 4B ..	988	0.55		
Direct Sky Blue FF ..	985	0.77	652	0.84
Direct Black EW	9,394	0.26	8,237	0.25
Direct Black RX	986	0.29	494	0.29
Direct Brown 3GO ..	1,347	0.33	864	0.34
Auramine	1,229	0.90	1,572	0.81
Methyl Violet B and Base	1,588	0.60	1,308	0.61
Nigrosine (spirit-soluble) ..	2,194	0.29	2,567	0.32
Nigrosine (water-soluble) ..	1,468	0.36	1,164	0.37
Sulfur Black	17,414	0.17	11,652	0.18

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[8] See p. 11.

[12] Synthetic Organic Chemicals, U.S. Production and Sales, 1941-43, U.S. Govt. Printing Office, Washington, 1946.

[13] Chemical Facts and Figures, Manufacturing Chemists Association of the United States, Washington, D.C., 1946.

Dye	1941		1945	
	Production 1000 pounds	*Unit value, $ per pound*	*Production 1000 pounds*	*Unit value, $ per pound*
Sulfur Blue	3,644	0.49	1,741	0.48
Sulfur Brown	2,885	0.27	1,747	0.28
Acid Alizarin Blue B ..	772	1.48	523	1.67
Anthraquinone Vat Yellow GC, 12½%	679	0.98	1,165	1.03
Anthraquinone Vat Golden Orange G, 12% ..	443	1.36	493	1.21
Anthraquinone Vat Dark Blue BO	368	1.15	519	1.29
Anthraquinone Vat Green B and Black B, 12½% ..	711	0.42	677	0.41
Anthraquinone Vat Violet 2R, 12½%	240	1.66	—	1.84
Anthraquinone Vat Blue RS, 10%			1,664	
Anthraquinone Vat Blue GCD, $8^{1}/_{3}$%	1,146	0.61	695	0.62
Anthraquinone Vat Blue BCS, 20%	1,835	1.05	1,193	—
Anthraquinone Vat Yellow G, 12½%	480	0.95	—	
Anthraquinone Vat Olive R, 12½%			3,386	1.12
Anthraquinone Vat Brown R, 12½%			1,670	1.22
Indigo, Synthetic, 20% ..	20,404	0.16	13,390	0.16
Bromindigo Blue 2BD, 16%	1,483	0.51	1,201	0.75
Vat Red 3B, 20%	346	0.97	198	1.05
Vat Orange R, 10% ..	459			
Indanthrene Brown RRD ..	459	1.09	654	0.98
Indanthrene Khaki 2G ..	2,092	1.15	6,571	1.21
Naphtol AS	886	0.93	806	0.96
Naphtol AS-D	68	1.92	91	1.98
Naphtol AS-SW	251	—	—	—

TABLE III

QUANTITIES AND VALUE OF SOME COAL-TAR INTERMEDIATES PRODUCED IN THE UNITED STATES IN 1941 AND 1945[13]

Intermediate	1941		1945	
	Production 1000 pounds	*Unit value, $ per pound*	*Production 1000 pounds*	*Unit value, $ per pound*
Acetanilide, tech	2,376		6,861	
6-Amino-1,3-naphthalenedisulfonic acid ..	1,581		1,106	
2-Amino-1-naphthalenesulfonic acid (Tobias acid)	2,346	0.53	1,834	0.52

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[13] See p. 14.

Intermediate	1941		1945	
	Production 1000 *pounds*	*Unit value,* $ *per pound*	*Production* 1000 *pounds*	*Unit value,* $ *per pound*
8-Amino-1,3,6-naphthalene-trisulfonic acid ..	4,521		3,283	
8-Amino-1-naphthol-5,7-disulfonic acid, monosodium salt (Chicago acid)	227		149	
8-Amino-1-naphthol-3,6-disulfonic acid, monosodium salt (H-acid) ..	4,226	0.36	3,923	
1-Amino-2-naphthol-4-sulfonic acid	1,172		1,120	
6-Amino-1-naphthol-3-sulfonic acid, sodium salt (J-acid)	1,036	1.81	691	1.98
7-Amino-1-naphthol-3-sulfonic acid, sodium salt (γ-acid)	1,354		1,018	
Aniline (Aniline oil) ..	70,009	0.11	87,195	0.10
Benzanthrone	639			
Benzidine hydrochloride and sulfate	1,889		1,878	
o-Benzoylbenzoic acid ..	4,708		7,665	
2-Chloroanthraquinone ..	909		976	
Chlorobenzene, mono ..	128,854	0.04	237,667	
Chlorobenzoylbenzoic acid	1,423		1,335	
1-Chloro-2,4-dinitrobenzene	12,908	0.12	14,123	
1-Chloro-2-methylanthraquinone	244		275	
α-Chlorotoluene (benzyl chloride)	3,367	0.17	5,054	0.18
Cresol (*ortho, meta, para*) ..	17,045	0.08	7,611	0.10
Cresylic acid, refined ..	26,596	0.07	20,896	0.08
1,5-Diaminoanthraquinone	355 (1942)			
Diaminoanthraquinone ..	328			
4,4′-Diamino-2,2′-stilbene-disulfonic acid	284		230	
o-Dichlorobenzene ..	7,755	0.06	11,843	0.06
2,5-Dichloroaniline ..	432	0.43	296	0.43
p-Dichlorobenzene	18,468	0.08	26,545	0.10
1,4-Dichloro-2-nitrobenzene	604		629	
Diethylaniline	671	0.40		
2,2′-Dimethyl-1,1′-dianthraquinonyl	126		156	
Dinitrobenzene	3,287			
N-Ethylaniline, mono and di	1,071	0.37	1,062	
3-Hydroxy-2-naphthoic acid	1,573	0.83		
Indophenol (blue and green)	546			
Metanilic acid	608		530	
p,p′-Methylenebis (*N,N′*-dimethylaniline)	1,135		1,465	

	1941		1945	
Intermediate	*Production 1000 pounds*	*Unit value, $ per pound*	*Production 1000 pounds*	*Unit value, $ per pound*
α-Naphthol	548	0.52	661	0.51
β-Naphthol, tech.	20,983			
2-Naphthol-3,6-disulfonic acid	720	0.49	594	
2-Naphthol-6,8-disulfonic acid	1,388	0.46	1,361	
1-Naphthol-4-sulfonic acid (Nevile and Winther's acid)	280			
2-Naphthol-6-sulfonic acid (Schaeffer acid)	312	0.44	195	
m-Nitroaniline	452	0.61	265	
5-Nitro-*o*-anisidine	250	1.81	131	
Nitrobenzene	94,945	0.07	116,203	0.07
p-Nitrosophenol	520		194	
Nitronaphthalene	5,287		5,968	
5-Nitro-*o*-toluenesulfonic acid	1,502	0.42	1,074	
2-Nitro-*p*-toluidine	959	0.97	744	1.02
Phenol, coal-tar	22,125	0.08	23,472	0.08
Phenol, synthetic	92,922	0.10	181,640	0.09
m-Phenylenediamine	1,164		1,010	
Phenylglycine, sodium salt	7,416		4,412	
Phenylmethylpyrazolone	557	1.14	87	0.98
Phthalic anhydride	81,309	0.14	125,033	0.13
Quinizarin (1,4-dihydroxy-anthraquinone)	395	1.39	1,092	1.48
Salicylic acid, tech.	9,894 (1942)	0.23		
Sulfanilic acid and salt	2,347		2,225	
1,4,5,8-Tetrakis-(1-anthraquinonylamino) anthraquinone	259		922	
o-Tolidine and salts	340		349	
4-(*o*-Tolylazo)-*o*-toluidine (*o*-aminoazotoluene)	588		437	
o-(*p*-Toluoyl) benzoic acid	590		649	
m-Toluylenediamine	1,701	0.65	591	
Trichlorobenzene	4,092	0.07	3,106	

The dyestuff industry at the present time is very wide in scope, and cannot be circumscribed within definable limits; for various economic, technical and historical reasons, it has come to be coextensive with the synthetic organic chemical industry. The raw materials and basic technology of the dyestuff industry are common to a great variety of organic chemicals and products. By-product coking and coal-tar distillation are the foundations on which the dyestuff industry is built, and in recent years petroleum has proved to be a useful source for the aromatic hydrocarbons. Starting from benzene, toluene, and other coal-tar primaries, over a thousand intermediates are made; and of the total weight of these intermediates, 15-20% is used in the manufacture of dyes and the remainder goes into other organic products. Synthetic drugs, photographic chemicals, rubber chemicals, and the miscellaneous products (" auxiliary agents " or assistants for wetting, dispersing, finishing and other purposes) required by the textile and other color-consuming industries, are natural corollaries to dyestuff manufacture; and a large dyestuff organization also includes within its orbit the technology of synthetic high polymers—rubber, plastics, and fibers. Further, in view of the quantities of sulfuric, hydrochloric and nitric acids, oleum, caustic soda and potash, ammonia, lime, soda ash, sodium sulfide, sodium nitrite, aluminium chloride, phosphorus and sulfur chlorides, sodium, sodamide and hydrogen used in the manufacture of intermediates and dyes, the dyestuff manufacturer is in practice, directly or through associated firms, a producer of inorganic heavy chemicals. The contact process for sulfuric acid and oleum, the electrolytic production of sodium, caustic soda and chlorine, and the synthesis of hydrochloric acid from hydrogen and chlorine, the fixation of atmospheric nitrogen and the manufacture of nitrogenous fertilizers, and several other inorganic chemicals and processes have originated partially or completely from the dyestuff industry. Dyes and intermediates thus constitute a " key industry" with which are unlocked a series of feeder, user and related industries, some of which surpass the dyestuff industry in their scale of operation and the money value of the products.

NAMES OF COMMERCIAL DYES

The same dye is marketed under a different name by each manufacturer, but in this book only one name has usually been mentioned, which may be the original name under which the dye was marketed or the best known name or the name which represents a dye of definite constitution. As a result of the last qualification, apart from the unquestionable fact that the Germans were the pioneer manufacturers of the great majority of dyes, there is a preponderance of IG names, since British and American reports on the German dyestuff industry have disclosed the constitution and method of preparation of a large number of IG dyes. The Color Index of the SDC, Schultz' Farbstofftabellen, and the Supplements to these volumes, list the commercial dyes and the available data regarding their constitution, methods of preparation, dyeing and fastness properties, and references to both the patent and scientific literature, brought up to 1928 (CI) and 1936 (Schultz). For dyes in the Color Index (abbreviated to CI) the number used in the Index is mentioned, so that further information including the names of commercial equivalents may be obtained if desired. The name of the discoverer or patentee and the date have also been cited for many dyes.

A difficulty with which the student of dyestuff chemistry is faced is the welter of names under which the same dyestuff may be known in commerce. The origin and significance of names such as Magenta, Congo Red, and Chicago Blue provide interesting speculation for the historian. Names of places in which the dyes were discovered or manufactured, names of flowers, and names which are euphonious, while also giving some indication of the chemical or dyeing character of a dyestuff, have all been utilized. There was fortunately some reduction in the number of commercial dyestuff names as a result of the amalgamation of dyestuff firms into large groups such as the IG and ICI after the first world war, although many of the names given by the component firms were still retained. The procedure now adopted by the main dyestuff firms is to assign a distinguishing name to a whole range of dyestuffs with a common method of application and similar fastness properties. Thus the names Durazol (ICI), Sirius (IG) and Chlorantine Fast (Ciba) are only applied to direct cotton colors with high fastness to light, and the name Indanthrene (IG) and Caledon (ICI) to vat colors with the highest all-round fastness. This class name is then followed by the name of the color and letters which show the shade of the color. The strength of the dyestuff in relation to a standard may also be stated. An example is Ponsol Brilliant Green 4G Double Paste ; Ponsol is the du Pont brand name for anthraquinonoid vat dyes ; Brilliant Green is the color; 4G stands for the yellowish (gelb) tone of the green; and double paste indicates the physical form of the dyestuff and the strength.[14]

CHEMICAL AND ENGINEERING ASPECTS OF DYESTUFF PRODUCTION

Dyestuff manufacture is extremely complex, on account of the great number and variety of the reactions, intermediates and final products. There are over 1,500 individual dyes in commerce, requiring over 1,000 intermediates. Among the long series of reactions are sulfonation, nitration, amination, catalytic reduction and oxidation, hydroxylation, alkylation, carboxylation, diazotization and coupling, cyclizations and condensations. Many of the reactions require the use of corrosive acids, caustic alkali and oxidizing agents, so that the plant has to be made of suitably resistant constructional material. Strong autoclaves are necessary for several reactions which have to be carried out at high pressure. There are toxic, explosion and fire hazards in handling some of the raw materials and intermediates, and stringent precautions in the operation of plant and processes have to be followed in dyestuff factories. In addition to the kettles, tanks and other equipment for the chemical reactions (or "unit processes"), the manufacture of intermediates and dyes requires a very wide range of plant for the "unit operations" of chemical engineering, such as evaporation, distillation, heat transfer, crystallization, filtration, drying, grinding and mixing.[15] The final and essential stage in the manufacture of a dyestuff is the standardization of shade, concentration and physical form on which depend the dyeing properties. In view of the number and character of the steps by which an aromatic hydrocarbon is converted into a dye, some variation in the purity of the dye from batch to batch is to be expected. Secondly, the desired range of shades may not be available from homogeneous dyes, and frequently a dye has therefore to be "shaded" with a second dye or sometimes even with two or three dyes, keeping in mind the need for the individual dyes in a mixture to have very similar dyeing and fastness properties. The diluents used in standardization should be such that they facilitate the application of the dyestuff, or at least are innocuous. Common diluents are sodium chloride, sulfate, bicarbonate and carbonate, and dispersing agents may be added if necessary. By use of suitable grinders, mixers, and homogenizers, commercial dyestuffs are ultimately produced as powders or pastes conforming to certain standards. A point to be emphasized in this connection is that the constitution assigned to a commercial dye refers to its essential or major tinctorial constituent; even so the constitution in some cases merely represents what is plausible. Publications based on careful experimental investigation are available for relatively few commercial dyes. The research departments of the large dyestuff organizations doubtless have much more precise knowledge of the composition and chemical constitution of commercial dyes, including dyes made by rival firms, than those outside the industry, but such information is usually not disclosed.

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[14] See Chapter VI for a further discussion and a list of commercial group names.

WORLD WAR II AND AFTER

On the defeat of Germany in the war, the Allied Control Council in Berlin in November 1945 seized all the property owned and controlled by the IG. Some of the plants were to be removed to allied countries as reparations; plants utilizable for war purposes were to be destroyed; and the ownership of the remaining plants and assets was to be dispersed, so that the IG could no longer function as a cartel. Ultimately a German production of dyes of 36,000 tons per year (50–55% of pre-war production) was to be permitted.

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[15] See books on chemical engineering; and German Chemical Industry with Special Reference to the Design of Plant for Dyestuffs and Intermediates, *BIOS* **1141**.

From June 1945 the allied countries have been sending out teams of investigators into Germany to inspect and report upon German industries. Several thousand reports of the British Intelligence Objectives Sub-Committee (BIOS) and the United States Field Intelligence Agency Technical (FIAT) have already been published, supplemented by numerous documents (copied, photographed or microfilmed). The printed reports and microfilms or photostatic copies of the documents are available for purchase, and the originals can be inspected at the Board of Trade German Division (Document Unit), Lansdowne House, Berkeley Square, London; and at the Department of Commerce, Office of Technical Services, Washington, D.C.

The IG, because of its size and influence in the German economy, has been reported upon very fully, and in view of the position occupied by the IG in the dyestuff industry of the world, the BIOS and FIAT reports and documents concerning the IG constitute the most comprehensive and authentic account which we have of the chemistry and technology of dyes, intermediates and related organic and inorganic chemicals. The chemistry of nearly the whole of the vast range of the dyes marketed by the IG, detailed production methods for thousands of the intermediates and dyes, and a great mass of information on IG research in the field, have now become available.[16]

The "development of new dyes and color application processes in Germany and Italy during world war II" has been described in BIOS Miscellaneous Report No. 20; but the title is not strictly accurate, since some of the dyes and application methods were released earlier. These advances are discussed later in connection with the relevant groups of dyes, and among them may be mentioned water-soluble dyes for acetate rayon on the model of the Solacet dyes (ICI); metallized azo dyes, not containing sulfonic groups, suitable for dyeing "Perlon", a synthetic polyamide fiber analogous to nylon; additions to the Benzo Fast Copper and the fast-to-light Sirius Supra ranges of direct cotton dyes, of which an example is the homogeneous green dye Sirius Supra Green BTL; a series of five new Benzo Fast Chrome dyes for dyeing union fabrics of wool and cellulose fibers; a new range of "Autazol Chrome dyes" for blue and black shades on union fabrics of wool and spun rayon; acid dyes of the triphenylmethane class containing alkysulfonic groups; Indanthrene Navy Blue RB (tetrachlorodibenzanthrone) and several Indanthrenes of the acridone and carbazole-acridone types; several Indigosols derived from anthraquinonoid vat dyes containing azo groups; Astrazon dyes, a new range of water-soluble dyes for acetate rayon, most of which are allied chemically to the cyanine dyes; and pigment printing colors in which water is the external phase in contrast with the Aridyes which are water-in-lacquer emulsions.

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[16] For an index of microfilms, see Robitschek, FIAT 764, 4 vols.

In FIAT Final Report 1313 comprising three volumes many processes for the manufacture of dyestuffs and dye intermediates developed by the German dyestuff industry are described. Analytical procedures and a review of dyestuff research subsequent to 1938 are included. The object of the investigating team, which consisted of nine experienced chemists and process engineers drawn from du Pont and GAFC and which was sent out in 1947, was to obtain additional information on dyestuffs and intermediates not covered by previous missions and recorded in BIOS, CIOS and FIAT reports.

The intense activity in dyestuff research and development outside Germany which began in 1920 was only interrupted when the second world war broke out in 1939. During the war the dyestuff firms were preoccupied with the large demand for a few khaki, olive and blue dyes, and with the utilization of the available plant and laboratory resources for war-time needs. The reconversion of the dyestuff industry to normal production has taken place rapidly and expansion programs appear to be well under way, so that the gap in the supply of dyes created by the dismemberment of the IG is becoming steadily smaller. The interval since the end of the war has been too short for new ground to be broken in dyestuff research, at least so far as patents and publications are concerned. Most of the work in dyestuff chemistry for many years has been carried out in the laboratories of the great dyestuff firms, and there is naturally a considerable time lag between discovery and publication. The patents released since 1945 therefore deal with research during the war and pre-war years, and in any case there has been nothing of a really novel or pioneering character. The Swiss firms for instance have a number of patents on direct cotton dyes converted in substance or on the fiber into copper complexes, which are merely variations on a well-known theme. The 2,4-diarylpyrroles from which a series of dyes of the methine or azamethine class have been prepared by ICI are more of an innovation. Progress in the anthraquinonoid vat dyes has been in the direction of improved methods of preparation of known intermediates and dyes, and modifications in the constitution of the established classes of dyes (e.g., the acylamidoanthraquinones, polyanthrimides and carbazoles, indanthrones and dibenzanthrones), rather than the discovery of new types. The use of phthalocyanine derivatives for textiles, which is receiving increasing attention, is a very promising line of advance. Chemists of the Eastman Kodak Co. have been active in two fields: dyes for cellulose acetate and cyanine dyes; in the latter field their work has included important contributions to color theory. Multiphase pigment emulsions containing resin binders were introduced for use in textile printing shortly before the war, and there has been considerable activity in this field with the objects of improving the fastness to rubbing and using such emulsions for dyeing. Quaternary ammonium salts and other compounds containing long paraffin chains have been known for some time to impart a more or less permanent finish to cellulose fabrics, although there is no evidence that these reagents interact with cellulose; a new approach to the fast dyeing of cellulose, which has always presented much more serious problems than the protein fibers, would be to synthesize dyes capable of stable chemical combination with the cellulose macromolecule. The dyeing of nylon and the newer fibers, and of mixed fibers, still presents difficulties, but the solution of most of them is within sight. Fastness demands, including fastness to new textile processing treatments, are becoming increasingly stringent, and a continued search for faster dyes produced at lower cost, which has been the chief object of the dyestuff manufacturer since the coal-tar color industry began, may be anticipated. Applicability by simple procedures yielding level shades in the shortest possible dyeing time, and suitability for the machinery and operations of a modern dyehouse, are other considerations in the commercial development of dyes. From the range of dyes already available it is clear that the discovery of new classes of synthetic dyes must necessarily be very difficult and infrequent in the future, but within the limits of the known chromophores and groups of dyes there is ample room for modifications leading to improvements in properties from the color users' point of view. On the theoretical side, curiously enough, color chemistry is almost a virgin field. Our knowledge of the relation between the chemical constitution of dyes and their color is largely empirical. The physicists have not yet been able to proceed beyond a few hydrocarbons in their application of quantum-mechanical methods to the interpretation and prediction of absorption spectra. Little is known of the precise action of light on dyes when fading takes place, and of any relation between the color and chemical constitution of a dye on the one hand and its fastness to light on the other. Concerning the catalytic activity of certain dyes in the photochemical degradation of cellulose, several problems remain unsolved. Theories of dyeing are in an extremely rudimentary condition, notwithstanding the spate of publications on the subject from time to time. Taking the single case of the affinity of the benzidine type of azo dye for cellulose, no decision has yet been possible on the kinetics of the absorption and the nature of the fiber-dye attachment in relation to the structure of the dye molecule.

CHAPTER II

RAW MATERIALS

The synthetic dyes are mainly derivatives of the aromatic hydrocarbons, benzene, toluene, naphthalene and anthracene, for which the chief source is coal tar. The term "synthetic dyes" has therefore been regarded in common usage as being synonymous with coal-tar dyes, but this is no longer strictly true, since the aromatic hydrocarbons are being manufactured in increasingly large quantities from petroleum. The tar obtained as a by-product in the production of coal gas, first carried out in England in 1814, was used only as a fuel until Hofmann in 1845 isolated benzene. The products of the carbonization or destructive distillation of coal are coal gas, a liquid condensate of ammonia and tar, and a solid residue of coke.[1] In spite of its very great value as a raw material for the dyestuff and other organic chemical industries, coal tar still remains a by-product in the sense that the primary object of distilling coal is the production of coal gas or of metallurgical coke. The yield and composition of tar depend on the character of the coal and on the technique of carbonization in which the important factors are the shape and size of the retorts, the rate of heating and the temperature and duration of the carbonization. The average coal for gas manufacture gives about 5-6% tar, whereas coking coal gives about 4% or less. A ton of coal thus yields 8–12 gallons of tar. The younger coals (lignite, brown coal) give tars which have a high content of paraffin hydrocarbons and are therefore of little use to the dye manufacturer. Bituminous coals with the minimum sulfur content give tars of particular value that do not contain excessive amounts of difficultly removable sulfur compounds. The temperature of carbonization usual in coke oven practice (1000–1250°) is favorable for the maximum yield of the simpler aromatic hydrocarbons and the naphthalene content of the tar is high. The total world production of coal tar is over 10 million tons, of which perhaps two-thirds are distilled.

Coal gas is passed through an efficient system of condensers and scrubbers in order to obtain the condensible products, which together constitute the tar; but the gas still contains considerable amounts of benzene and toluene, and these are recovered by washing the gas with the heavy oil fraction of coal tar mentioned later. In fact, two to three times as much benzene and toluene are obtained from the gas as from the tar.

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[1] For full accounts of coal carbonization and tar distillation, see Lowry, Chemistry of Coal Utilization, Vol. I and II, Wiley, New York, 1945.

Coal tar, a viscous liquid of sp. gr. 1.05–1.3, is black in color because it is a dispersion of carbon in an oil.[2] The oil consists of a mixture of hundreds of compounds, and many more are formed during the distillation of the tar. Several hundreds of these compounds have been identified,[3] and over three hundred have so far been isolated in pure form and characterized (see Charts 1 and 2 and Table I). The aromatic hydrocarbon constituents vary in complexity from benzene to chrysene ($C_{18}H_{12}$) and picene ($C_{22}H_{14}$). There are also present phenols and acids, nitrogenous substances such as pyridine and quinoline, and sulfur compounds such as thiophene. The important substances from the point of view of dyestuff manufacture are benzene, toluene, xylenes, naphthalene, anthracene, acenaphthene, and pyrene among the hydrocarbons; pyridine and carbazole; phenol and the cresols; others in Chart 2 are of minor interest. Table II gives the analyses of two tars produced in typical by-product coke oven installations in the United States, the quantities mentioned being regarded as commercially recoverable.[4]

Among the coal-tar constituents mentioned in Table I will be recognized several well-known dye intermediates such as aniline, α- and β-naphthol; but these occur in such small amounts that their separation from coal tar is not commercially feasible and they are made from the relevant hydrocarbons by synthetic processes. On the other hand, the scale on which tar distillation is carried out in a few places, the great efficiency of the primary and subsequent distillations, and the refinements of fractional separation in modern chemical engineering practice have made it possible to isolate an increasing number of coal-tar chemicals in commercial quantities. Kruber, Spilker and other chemists of Gesellschaft für Teerverwertung at Duisberg-Meiderich in Germany have been largely responsible for the isolation of the less known constituents of coal tar.[5] Chart 1 lists the compounds which can be isolated from coal tar by technically feasible processes, although many of these are not normally produced on account of the cost and the limited demand. Among the coal-tar products which have become available in recent years may be mentioned methyl- and dimethylnaphthalenes, fluorene, fluoranthene, indene, pyrene, chrysene, α-picoline, collidine, 2-methylindole, acridine, and several of the xylenols.

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[2] The insoluble matter of coal tar has been examined by Green, Ward, and Thakur, *J. Soc. Chem. Ind.* **67,** 422 (1948).

[3] Rhodes, O'Brochta and Wooldridge *in* Lowry, Chemistry of Coal Utilization, Vol. II, Wiley, New York, 1945, have listed 348 " compounds identified from the carbonization of coal " together with their physical properties, an indication of their occurrence in high or low temperature tar, and references to the original literature.

[4] Lowry, Chemistry of Coal Utilization, Vol. II, Wiley, New York, 1945, p. 1327.

[5] *BIOS* **941.**

CHART 1

CONSTITUENTS ISOLABLE FROM COAL TAR

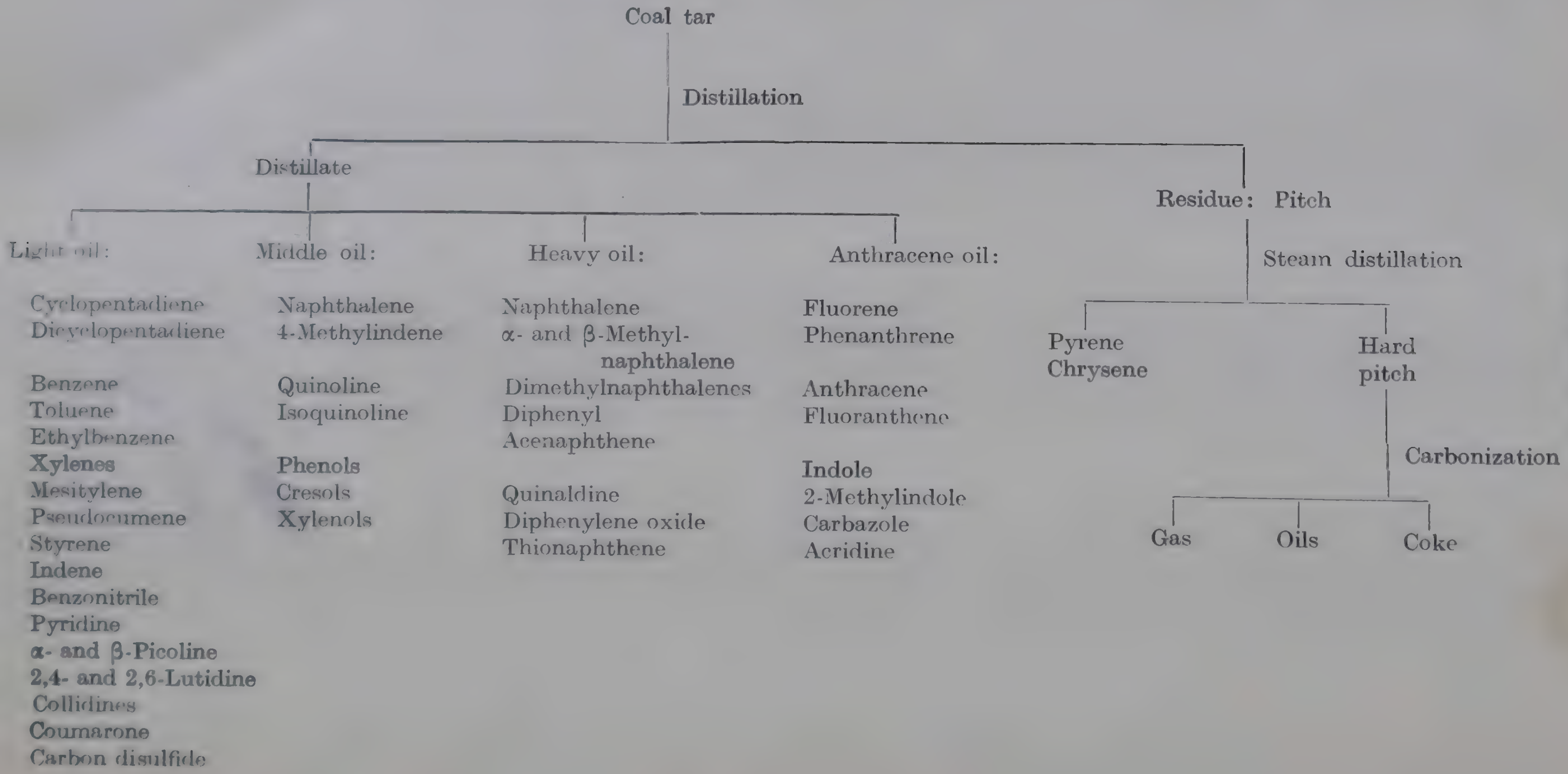
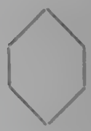

Coal tar
Distillation
Distillate
Residue: Pitch
Light oil:
Cyclopentadiene
Dicyclopentadiene
Benzene
Toluene
Ethylbenzene
Xylenes
Mesitylene
Pseudocumene
Styrene
Indene
Benzonitrile
Pyridine
α- and β-Picoline
2,4- and 2,6-Lutidine
Collidines
Coumarone
Carbon disulfide
Middle oil:
Naphthalene
4-Methylindene
Quinoline
Isoquinoline
Phenols
Cresols
Xylenols
Heavy oil:
Naphthalene
α- and β-Methylnaphthalene
Dimethylnaphthalenes
Diphenyl
Acenaphthene
Quinaldine
Diphenylene oxide
Thionaphthene
Anthracene oil:
Fluorene
Phenanthrene
Anthracene
Fluoranthene
Indole
2-Methylindole
Carbazole
Acridine
Steam distillation
Pyrene
Chrysene
Hard pitch
Carbonization
Gas
Oils
Coke

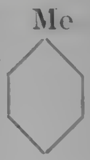
CHART 2

COAL-TAR CONSTITUENTS USED IN THE DYESTUFF INDUSTRY.

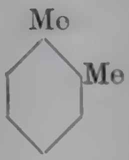
1. *Aromatic hydrocarbons*:



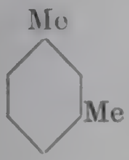
Benzene
m.p. 5.5°
b.p. 80.1 °



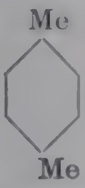
Toluene
m.p. −95°
b.p. 110.8°



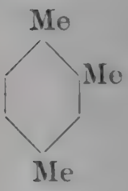
o-Xylene
b.p. 144°



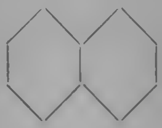
m-Xylene
b.p. 139.3°



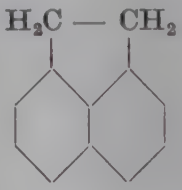
p-Xylene
b.p. 139.4°



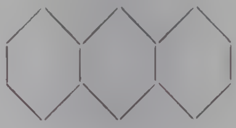
Pseudocumene
b.p. 169.2°



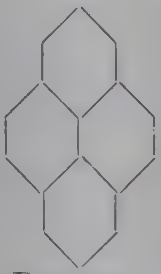
Naphthalene
m.p. 80°
b.p. 218°



Acenaphthene
m.p. 96°
b.p. 280.7°

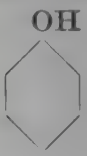


Anthracene
m.p. 217°
b.p. 342.3°

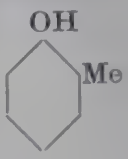


Pyrene
m.p. 148°
b.p. 393°

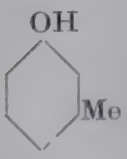
2. *Phenols and their derivatives* :



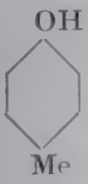
Phenol
m.p. 41°
b.p. 181°



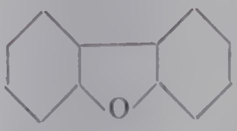
o-Cresol
m.p. 31°
b.p. 191°



m-Cresol
m.p. 10.9°
b.p. 202°

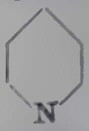


p-Cresol
m.p. 36°
b.p. 201°

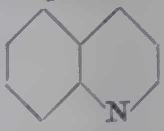


Diphenylene oxide
m.p. 83°
b.p. 287°

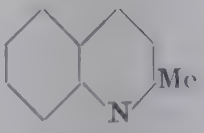
3. *Nitrogen-containing compounds* :



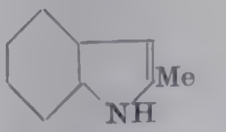
Pyridine
m.p. −42°
b.p. 115°



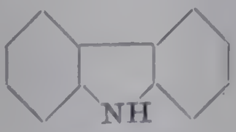
Quinoline
m.p. −15°
b.p. 238°



Quinaldine
m.p. −2°
b.p. 247.6°



2-Methylindole
m.p. 61°
b.p. 271—272°



Carbazole
m.p. 244.8° b.p. 352°

TABLE I

AROMATIC COMPOUNDS PRESENT IN COAL TAR ARRANGED IN ORDER OF B.P.

	Name	*Formula*	*B.P.* °C.	*M.P.* °C.
1.	Benzene	C_6H_6	80.1	5.51
2.	Thiophene	C_4H_4S	84.0	
3.	Toluene	C_7H_8	110.8	
4.	2-Methylthiophene (Thiotolene)	C_5H_6S	112-113	
5.	3-Methylthiophene	C_5H_6S	114	
6.	Pyridine	C_5H_5N	115	—42
7.	α-Picoline	C_6H_7N	129	—69.9
8.	An azulene	$C_{15}H_{18}$	130/12 mm.	
9.	Pyrrole	C_4H_5N	131	
10.	Ethylbenzene	C_8H_{10}	136.15	
11.	Dimethylthiophene (Thioxene)	C_6H_8S	137	
12.	*m*-Xylene	C_8H_{10}	139.3	
13.	*p*-Xylene	C_8H_{10}	139.4	
14.	*o*-Xylene	C_8H_{10}	144	
15.	β-Picoline	C_6H_7N	144	—18 3
16.	2,6-Dimethylpyridine (2,6-Lutidine)	C_7H_9N	144.4	—6
17.	γ-Picoline	C_6H_7N	144.6	3.8
18.	Styrene	C_8H_8	146	
19.	Cumene	C_9H_{12}	153	
20.	2,4-Dimethylpyridine	C_7H_9N	157	
21.	2,5-Dimethylpyridine	C_7H_9N	159.5	
22.	*n*-Propylbenzene	C_9H_{12}	159.5	
22a.	2-Methyl-6-ethylpyridine	$C_8H_{11}N$	160–161	
23.	*m*-Ethyltoluene	C_9H_{12}	162	
24.	*p*-Ethyltoluene	C_9H_{12}	162	
25.	2,3-Dimethylpyridine	C_7H_9N	162–163	
26.	Trimethylthiophene	$C_7H_{10}S$	163	
27.	3,4-Dimethylpyridine	C_7H_9N	163.5–164.5	
28.	Mesitylene (1,3,5-Trimethylbenzene)	C_9H_{12}	164.6	
29.	*o*-Ethyltoluene	C_9H_{12}	164.9	
30.	4-Ethylpyridine	C_7H_9N	165	
31.	2,4,5-Trimethylpyridine	$C_8H_{11}N$	167	
32.	2,3,4-Trimethylpyridine	$C_8H_{11}N$	168	
33.	Pseudocumene (1,2,4-Trimethylbenzene)	C_9H_{12}	169.18	
34.	Thiophenol	C_6H_6S	169.5	
35.	3,5-Dimethylpyridine	C_7H_9N	169.5	
36.	2,4,6-Trimethylpyridine	$C_8H_{11}N$	171	
37.	2,3,6-Trimethylpyridine	$C_8H_{11}N$	173-174	
38.	Coumarone	C_8H_6O	173-175	
39.	Hemimellitene (1,2,3-Trimethylbenzene)	C_9H_{12}	176.1	
40.	Cymene (*p*-Methylisopropylbenzene)	$C_{10}H_{14}$	177	
41.	Hydrindene	C_9H_{10}	178	
42.	Phenol	C_6H_6O	181	41
43.	Indene	C_9H_8	182	—2
44.	Tetramethylthiophene	$C_8H_{12}S$	183	

	Name	*Formula*	*B.P.* °*C.*	*M.P.* °*C.*
45.	Aniline	C_6H_7N	184	—6
46.	2,3,5-Trimethylpyridine	$C_8H_{11}N$	186.75	
47.	3,4-Dimethylethylbenzene	$C_{10}H_{14}$	189	
48.	3,5-Dimethylethylbenzene	$C_{10}H_{14}$	ca.190	
49.	6-Methylcoumarone	C_9H_8O	190-191	
50.	*o*-Cresol	C_7H_8O	191	31
51.	Benzonitrile	C_7H_5N	191	—13
52.	Tolylmercaptan	C_7H_8S	ca.195	
53.	3, or 5-Methylcoumarone	C_9H_8O	195–196	
54.	Durene (1,2,4,5-Tetramethylbenzene)	$C_{10}H_{14}$	196	
55.	4-Methylcoumarone	C_9H_8O	197–199	
56.	Isodurene (1,2,3,5-Tetramethylbenzene)	$C_{10}H_{14}$	198	
57.	1,2-Dimethyl-4-isopropylbenzene	$C_{11}H_{16}$	199	
58.	*p*-Toluidine	C_7H_9N	200.4	45
59.	*o*-Toluidine	C_7H_9N	200.7	—24.4
60.	*p*-Cresol	C_7H_8O	201	36
61.	Acetophenone	C_8H_8O	202	20
62.	*m*-Cresol	C_7H_8O	202	10.9
63.	4-Methylhydrindene	$C_{10}H_{12}$	203	
64.	*m*-Toluidine	C_7H_9N	203.3	
65.	Prehinitene (1,2,3,4-Tetramethylbenzene)	$C_{10}H_{14}$	204.5	
66.	4-Methylindene	$C_{10}H_{10}$	205	
67.	*o*-Ethylphenol	$C_8H_{10}O$	206.5-207	
68.	Tetrahydronaphthalene	$C_{10}H_{12}$	206.8	
69.	*m*-4-Xylenol	$C_8H_{10}O$	209	26
70.	*m*-2-Xylenol	$C_8H_{10}O$	211.2	49
71.	*p*-2-Xylenol	$C_8H_{10}O$	211.5	74.5
72.	*m*-4-Xylidine	$C_8H_{11}N$	212	
73.	*m*-Ethylphenol	$C_8H_{10}O$	214	52
74.	*p*-2-Xylidine	$C_8H_{11}N$	215	
75.	*p*-Ethylphenol	$C_8H_{10}O$	218	45
76.	Naphthalene	$C_{10}H_8$	218	80
77.	*o*-3-Xylenol	$C_8H_{10}O$	218	73–75
78.	*m*-5-Xylenol	$C_8H_{10}O$	219.5	68
79.	Mesitol	$C_9H_{12}O$	219.5	68–69
80.	*m*-5-Xylidine	$C_8H_{11}N$	220–221	
81.	3,6-Dimethylcoumarone	$C_{10}H_{10}O$	220–222	
82.	4,5-Dimethylcoumarone	$C_{10}H_{10}O$	220-222	
83.	4,6-Dimethylcoumarone	$C_{10}H_{10}O$	220–222	
84.	*p*-Methyl tolyl ketone	$C_9H_{10}O$	222	
85.	Thionaphthene	C_8H_6S	222	32
86.	*o*-3-Xylidine	$C_8H_{11}N$	223	
87.	*o*-4-Xylenol	$C_8H_{10}O$	225	65
88.	Dimethylindene	$C_{11}H_{12}$	225–230	
89.	4,6-Dimethylhydrindene	$C_{11}H_{14}$	226–232	
90.	Pseudocumenol (2,4,5-Trimethylphenol)	$C_9H_{12}O$	232	71
91.	3-Methyl-5-ethylphenol	$C_9H_{12}O$	232.5–234.5	55
92.	2,3,4,5-Tetramethylpyridine	$C_9H_{13}N$	233	

	Name	*Formula*	*B.P.* °C.	*M.P* °C.
93.	Isopseudocumenol (2,3,5-Trimethylphenol)	$C_9H_{12}O$	233	96
94.	Quinoline	C_9H_7N	238	—15
95.	Isohomocatechol (2,3-Dihydroxytoluene)	$C_7H_8O_2$	d. 239	47
96.	7-Hydroxycoumarone	$C_8H_6O_2$	240	43
97.	Methylthionaphthene	C_9H_8S	240–245	
98.	2-Methylnaphthalene	$C_{11}H_{10}$	241.14	34.44
99.	Isoquinoline	C_9H_7N	243.25	28
100.	1-Methylnaphthalene	$C_{11}H_{10}$	244.78	—30.9
101.	4-Hydroxyhydrindene	$C_9H_{10}O$	245	50
102.	Catechol	$C_6H_6O_2$	245	105
103.	2-Methylquinoline (Quinaldine)	$C_{10}H_9N$	247.6	—2
104.	8-Methylquinoline	$C_{10}H_9N$	247.75	
105.	3,4,5-Trimethylphenol	$C_9H_{12}O$	248	106
106.	Durenol (2,3,5,6-Tetramethylphenol)	$C_{10}H_{14}O$	248	119
107.	Benzoic acid	$C_7H_6O_2$	249	121
108.	Guaiacol	$C_7H_8O_2$	250	28
109.	Homocatechol (3,4-Dihydroxytoluene)	$C_7H_8O_2$	251	65
110.	5-Hydroxyhydrindene	$C_9H_{10}O$	251	
111.	2-Ethylnaphthalene	$C_{12}H_{12}$	252	—7.5
112.	1-Ethylnaphthalene	$C_{12}H_{12}$	252	—15
113.	3-Methylisoquinoline	$C_{10}H_9N$	252.25	64.7
114.	Indole	C_8H_7N	253	52.5
115.	Dimethylcatechol	$C_8H_{10}O_2$	253	
116.	Diphenyl	$C_{12}H_{10}$	255.2	71
117.	1-Methylisoquinoline	$C_{10}H_9N$	255.25	10.1
118.	2,8-Dimethylquinoline	$C_{11}H_{11}N$	255.25	23.2
119.	7-Methylquinoline	$C_{10}H_9N$	257.6	39
120.	6-Methylquinoline	$C_{10}H_9N$	258.6	ca. —22
121.	*o*-Toluic acid	$C_8H_8O_2$	259.2	103.7
122.	3-Methylquinoline	$C_{10}H_9N$	259.55	16–17
123.	2,6-Dimethylnaphthalene	$C_{12}H_{12}$	260.5	110
124.	2,7-Dimethylnaphthalene	$C_{12}H_{12}$	262	97
125.	1,7-Dimethylnaphthalene	$C_{12}H_{12}$	262	
126.	1,3-Dimethylisoquinoline	$C_{11}H_{11}N$	262.4	29.8–30
127.	1,6-Dimethylnaphthalene	$C_{12}H_{12}$	262.5	
128.	5-Methylquinoline	$C_{10}H_9N$	262.7	19
129.	4-Methylquinoline	$C_{10}H_9N$	264. 2	9–10
130.	5- or 7-Methylisoquinoline (probable)	$C_{10}H_9N$	264.9	76
131.	3-Methylindole (Skatole)	C_9H_9N	265	95
132.	1,5-Dimethylnaphthalene	$C_{12}H_{12}$	265–265.5	80–80.5
133.	6-Methylisoquinoline (probable)	$C_{10}H_9N$	265.5	85–86
134.	7-Methylindole	C_9H_9N	266	85
135.	2,3-Dimethylnaphthalene	$C_{12}H_{12}$	266	104.5
136.	1,2-Dimethylnaphthalene	$C_{12}H_{12}$	266–267	—3.5
137.	4-Methylindole	C_9H_9N	267	5
138.	5-Methylindole	C_9H_9N	267	60
139.	3-Methyldiphenyl	$C_{13}H_{12}$	269	

	Name	*Formula*	*B.P.* °C.	*M.P.* °C.
140.	5,8-Dimethylquinoline	$C_{11}H_{11}N$	> 270	
141.	4-Methyldiphenyl	$C_{13}H_{12}$	271	48
142.	2-Methylindole	C_9H_9N	271–272	61
143.	*o*-Phenylphenol	$C_{12}H_{10}O$	275	67.5
144.	Resorcinol	$C_6H_6O_2$	276.5	111.6
145.	1,3,7-Trimethylnaphthalene	$C_{13}H_{14}$	280	13.5
146.	α-Naphthol	$C_{10}H_8O$	280	94
147.	Acenaphthene	$C_{12}H_{10}$	280.7	96
148.	α-Naphthofuran	$C_{12}H_8O$	282–284	
149.	β-Naphthofuran	$C_{12}H_8O$	284–286	50–51
150.	2,3,5-Trimethylnaphthalene	$C_{13}H_{14}$	285	25.3
151.	Hydroquinone	$C_6H_6O_2$	285	172.3
152.	2,3,6-Trimethylnaphthalene	$C_{13}H_{14}$	286	102.0
153.	β-Naphthol	$C_{10}H_8O$	286	123
154.	Diphenylene oxide	$C_{12}H_8O$	287	83
155.	2,4,6-Trimethylquinoline	$C_{12}H_{13}N$	288	50
156.	3,4-Dimethyldiphenyl	$C_{14}H_{14}$	289	14
157.	4,4′-Dimethyldiphenyl	$C_{14}H_{14}$	292	122
158.	4,5-Benzindane	$C_{13}H_{12}$	295	
159.	1-Naphthonitrile	$C_{11}H_7N$	297	34
160.	1-Methyldiphenylene oxide	$C_{13}H_{10}O$	298	45
161.	Fluorene	$C_{13}H_{10}$	298	115
162.	9, 10-Dihydroacridine	$C_{13}H_{11}N$	d. 300	169
163.	1-Naphthylamine	$C_{10}H_9N$	301	
164.	2-Methyldiphenylene oxide	$C_{13}H_{10}O$	303–304	66
165.	2-Naphthonitrile	$C_{11}H_7N$	304	67
166.	2-Naphthylamine	$C_{10}H_9N$	306	
167.	2-Methylfluorene	$C_{14}H_{12}$	318	104
168.	3-Methylfluorene	$C_{14}H_{12}$	318	85
169.	*p*-Phenylphenol	$C_{12}H_{10}O$	319	
170.	Diphenylene sulfide	$C_{12}H_8S$	332	97
171.	Phenanthrene	$C_{14}H_{10}$	340	100
172.	Tetramethylbiphenol	$C_{16}H_{18}O_2$	341	
173.	Anthracene	$C_{14}H_{10}$	342.3	217
174.	Acridine	$C_{13}H_9N$	346	110
175.	2-Hydroxydiphenylene oxide	$C_{12}H_8O_2$	348	143
176.	Phenanthridine	$C_{13}H_9N$	349	106
177.	3-Methylphenanthrene	$C_{15}H_{12}$	350	65
178.	Carbazole	$C_{12}H_9N$	352	244.8
179.	2-Hydroxyfluorene	$C_{13}H_{10}O$	ca. 352	
180.	4,5-Phenanthrylenemethane	$C_{15}H_{10}$	353	116
181.	9-Methylphenanthrene	$C_{15}H_{12}$	354–355	92
182.	1-Methylphenanthrene	$C_{15}H_{12}$	354–355	119
183.	2-Phenylnaphthalene	$C_{16}H_{12}$	357–358	103
184.	Hydroxyanthracene	$C_{14}H_{10}O$	d. 360	
185.	Naphthacene	$C_{18}H_{12}$	> 360	
186.	2-Methylanthracene	$C_{15}H_{12}$	> 360	202
187.	2,7-Dimethylanthracene	$C_{16}H_{11}$	> 360	241
188.	2,6-Dimethylanthracene	$C_{16}H_{14}$	> 360	250
189.	2,3,6-Trimethylanthracene	$C_{17}H_{16}$	> 360	245
190.	2,3,6,7-Tetramethylanthracene	$C_{18}H_{18}$	> 360	
191.	2,6-Dimethylnaphthacene	$C_{20}H_{16}$	> 360	341

	Name	*Formula*	*B.P.* °C.	*M.P.* °C.
192.	2-Methylcarbazole	$C_{13}H_{11}N$	363	259
193.	1,2,3,4-Tetrahydrofluoranthene	$C_{16}H_{14}$	363–365	76
194.	3-Methylcarbazole	$C_{13}H_{11}N$	365	207
195.	Fluoranthene	$C_{16}H_{10}$	382	109
195a.	2-Azafluoranthene	$C_{15}H_{9}N$	388	83
196.	2,3,5,6-Dibenzocoumarone	$C_{16}H_{10}O$	392–397	205
197.	Pyrene	$C_{16}H_{10}$	393	148
198.	1,9-Benzoxanthene	$C_{16}H_{10}O$	395	
199.	2-Hydroxyphenanthrene	$C_{14}H_{10}O$	396	168–169
200.	Retene (8-Methyl-2-isopropyl-phenanthrene)	$C_{18}H_{18}$	398.8	
201.	1,2-Benzofluorene	$C_{17}H_{12}$	413	189–190
202.	2,3-Benzofluorene	$C_{17}H_{12}$	415	208–209
203.	Naphtho-2′,3′–,1,2–anthracene	$C_{22}H_{14}$	>424	
204.	1,2-Benzonaphthacene	$C_{22}H_{14}$	>425	
205.	Phenanthridone	$C_{13}H_{9}NO$	435	293
206.	Dibenzothionaphthene	$C_{16}H_{10}S$	ca. 440	
207.	Chrysene	$C_{18}H_{12}$	448.5	255
208.	Triphenylene	$C_{18}H_{12}$	450	197
209.	2,3-Benzocarbazole	$C_{16}H_{11}N$	ca. 450	ca. 330
210.	Benzerythrene	$C_{24}H_{18}$	>500	317
211.	1,2-Benzanthracene	$C_{18}H_{12}$	500–510	160
212.	Perylene	$C_{20}H_{12}$	500–510	273–274
213.	4,5-Benzopyrene	$C_{20}H_{12}$	500–510	179
214.	1,2-Benzopyrene	$C_{20}H_{12}$	500–510	177
215.	Picene	$C_{22}H_{14}$	519	364

TABLE II

ANALYSIS OF TWO TYPICAL COKE OVEN TARS

	Tar 1 %	*Tar 2* %
Benzene	0.293	0.079
Toluene	0.129	—
Solvent naphtha	1.667	0.726
Coumarone resin	0.047	0.071
Benzoic acid	0.043	0.053
Phenol	0.861	0.469
Cresols	1.822	0.735
Pyridine	0.128	0.050
High-boiling bases	0.083	0.051
Naphthalene	4.801	8.273
β-Methylnaphthalene	0.142	0.300
Quinoline (technical)	0.247	0.236
Acenaphthene	1.129	1.510
Fluorene	0.902	0.847
Phenanthrene	2.900	3.388
Anthracene	0.705	1.157
Carbazole	0.623	0.706
	16.522	18.651
Light-oil constituents	2.179	0.929
True coal-tar constituents	14.343	17.722

Another example[6] is the profitable recovery of benzoic acid by the saponification of benzonitrile occurring to the extent of 0.6% in the solvent naphtha fraction. Chart 2 gives the structural formulas of the coal-tar constituents which are employed as raw materials for the dyestuff industry.

The separation of the tar into the desired constituents[7] is effected by a series of physical operations: fractional distillation, cold and hot pressing, crystallization, and sublimation; but the purification also involves chemical treatments such as acid and alkali extractions. Before the tar is distilled, careful and complete dehydration is necessary to avoid bumping and frothing. The distillation[8, 9] is carried out in wrought-iron or mild-steel pot stills of about 15-20 tons capacity, preferably provided with a hollow agitator through which steam can be blown for facilitating the distillation of the heavy oils at a later stage of the distillation; agitators are particularly necessary for high-carbon coal tars which might cake on the hotter parts of the shell. The goose neck of the still is connected to a condensing worm, from which the distillates are conducted to a series of receivers. The fractions are collected on the basis of b.p.'s or the sp. gr. of the distillates. The number of fractions and their boiling ranges vary considerably in different tar distilleries and typical figures are recorded in Table III.

TABLE III

Fraction	*B.P.*	*Sp. gr.*	*Per cent of tar*
Light oil			
First runnings	Up to 110°	0.92–0.95	1–4
Naphtha	110–180°		
Middle or carbolic oil	180–240°	0.98–1.02	3–10
Heavy or creosote oil	240–270°	1.03–1.04	6–12
Anthracene oil	270–360°	1.1	13–25
Pitch			55–60

Since the division into light, middle, heavy and anthracene oils is arbitrary, and the b.p.'s between which the cuts are made vary considerably, a compound noted in Chart 1 as occurring in one of the four fractions may be found instead or also in another. Another feature of coal-tar constituents is the formation of molecular compounds as a result of which a substance with a certain b.p. may actually be isolated from a fraction of higher b.p. range.

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[6] *BIOS* **940.**

[7] German tar distillery practice is described in the following *BIOS* reports: **331,332, 450, 507, 560, 596, 834, 934, 936, 939, 940, 941, 942, 1117**; and in *CIOS* report Item **30,** File XXXII-93.

[8] For a brief but comprehensive account of tar distillation processes, see Potter in Thorpe's Dictionary of Applied Chemistry, 4th ed., Vol. III, Longmans, London, 1939, p. 209.

[9] For a detailed survey of the history and practice of the tar distillation industry, see Adam, *J. Junior Inst. Engrs. London* **55,** 325 (1945).

While batch distillation in pot or longitudinal stills continues to be practised, continuous processes using pipe or coil stills similar to those commonly employed in the petroleum industry are also largely used. In the Koppers process used in Germany[10], dehydrated tar is passed through a pipe still consisting of a nest of tubes (80 mm. diameter) in a chamber heated by coke oven gas. The tar from the still, which is at atmospheric pressure and a temperature of 320°, enters a column where the pressure drops to 80–100 mm. and the temperature to 280°, so that the vapors are flashed off. Pitch runs off at the bottom of the column, and the other fractions are collected in the reverse order in comparison with the usual process of fractional distillation. The vapors pass through a series of columns and condensers; anthracene oil (wash oil used for stripping benzene and toluene from coal gas), naphthalene oil, and carbolic oil separate in this order, and the light oils are finally condensed.

Each of the five or six fractions is redistilled from stills provided with suitable fractionating columns. The light oil, the bulk of which comes from the gas, is thus divided into (1) crude benzene, (2) crude toluene, (3) crude xylene (solvent naphtha), and (4) the still bottoms (" dead oil "). The next stage consists of chemical treatments. Crude benzene and toluene[11] are washed with 7–10% caustic soda solution to dissolve phenols, and then with dilute sulfuric acid to dissolve pyridine and other bases; phenols, pyridine and quinoline are subsequently recovered from these extracts. Unsaturated hydrocarbons and sulfur compounds (chiefly thiophene) are then removed from the benzene fraction by agitation with concentrated sulfuric acid, which partly solubilizes and partly resinifies these impurities; the strong acid treatment is omitted in the case of toluene to avoid loss by sulfonation. It has been stated that sulfur as carbon disulfide is best removed by extraction with a solution of sodium polysulfide. A method for removing thiophene from benzene is to add an indene fraction prior to sulfuric acid treatment.[12] The hydrocarbons are finally washed with dilute alkali and water, and distilled using fractionating columns and dephlegmators which enable very close fractionation to be effected. From the benzene fraction the first runnings are carbon disulfide, collected and sold to viscose manufacturers. Pure benzene and pure toluene are collected within a range of half a degree of the correct boiling point. Benzene and toluene, as primary materials for dyes, explosives and organic fine chemicals, have to conform to stringent standards of purity which are outlined later.

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[10] *BIOS* **596.**

[11] The aromatic hydrocarbons, as well as their chloro and other derivatives, can lead to toxic effects by inhalation and by absorption through the skin, and care is necessary in their industrial use (see Lehmann and Flury, Toxicology and Hygiene of Industrial Solvents, Williams and Wilkins, Baltimore, 1943).

[12] *FIAT* **729.**

Apart from pure benzene and toluene, "motor benzole" of various b.p. ranges is produced on a large scale for use as fuel. According to the percentage distilling below 100° with the bulb of the thermometer in the liquid, these benzoles are marketed as 90's, 50's . . . and 0's benzole. The composition of 90's benzole, for instance, is benzene 84, toluene 13, and xylenes 3%.

Crude xylene or solvent naphtha, which may contain 2–15% of *o*-xylene, 70–85% of *m*-xylene, 3–10% of *p*-xylene, and 3–10% of paraffins, is useful as a solvent. For the rubber industry in which it is extensively used, a finished solvent distilling at 120–160° is produced; as a special solvent in the paint and lacquer industries, a mixture of the three isomeric xylenes boiling within a range of 2–5° is separated. For use as raw materials in the dyestuff industry, separation into pure *o*-, *m*-, and *p*-xylene is necessary. Until recently the *m*-isomer was used mainly, the *p*-isomer being next in importance; but the position is now different on account of the development of a process for the manufacture of phthalic anhydride from *o*-xylene. Since the *o*-, *m*-, and *p*-isomers boil respectively at 144, 139.3 and 139.4°, they cannot be separated by fractional distillation. Isolation of *m*-xylene alone can be accomplished by treatment with boiling dilute nitric acid under conditions in which the *m*-xylene is not attacked, whereas *o*- and *p*-xylenes are oxidized to phthalic and terephthalic acids. Each of the three isomers can be isolated by sulfonation with cold concentrated sulfuric acid when *p*-xylene is unaffected. The acid layer is diluted, neutralized with caustic soda, and the sodium sulfonates of *o*- and *m*-xylene separated by fractional crystallization. By dissolving the sodium sulfonate in concentrated sulfuric acid and passing superheated steam, the sulfonic group is split off and the hydrocarbon distils.[13] The *m*- and *p*-isomers

$$\mathrm{ArSO_3H + H_2O \longrightarrow ArH + H_2SO_4}$$

can be separated from a mixture by dilution with a relatively volatile diluent (e.g., methanol, acetone) having a freezing point below −58.5° (the eutectic point for *m*- and *p*-xylenes); the diluted mixture is cooled until most of the *p*-xylene has crystallized.[14]

The fraction boiling between 160 and 190°, which is obtained partly from the light oil and partly from the middle oil after removal of naphthalene and phenols as mentioned later, contains *p*-ethyltoluene (b.p. 162°), mesitylene (b.p. 164.6°), 1,2,4-trimethylbenzene (pseudocumene; b.p. 169.2°), coumarone (b.p. 173-175°), and indene (b.p. 182°). Pseudocumene is the only constituent of this fraction which is used (to a very minor extent) in making dye intermediates. By fractional distillation a narrow cut (e.g., between 165° and 175°) is taken and treated with concentrated sulfuric acid. Mesitylene remains unattacked, while coumarone polymerizes to an amber-colored resin, which, after distillation, is a pale material of m.p. 50–60°. The polymer is used in the varnish industry. Pseudocumene and *p*-ethyltoluene undergo sulfonation and dissolve; and the sulfonic acids are separated by taking advantage of their difference in solubility in 50% sulfuric acid, pseudocumenesulfonic acid being much less soluble. The hydrocarbons are then regenerated by hydrolysis of the sulfonic acids.

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[13] Clarke and Taylor, *JACS* **45,** 830 (1923); Löfgren, *Svensk Kem. Tid.* **60,** 281 (1948).

[14] Arnold, BP 585,076.

From the solvent naphtha fraction boiling at about 180°, benzoic acid and indene can also be recovered. Benzonitrile (b.p. 191°) is present in this fraction, and can be obtained as benzoic acid by saponification with strong alkali. If the treated naphtha is fractionated, and the cut at 181–182° is heated with about 10% of its weight of metallic sodium at 165°, indene separates as the sodium compound, from which the hydrocarbon is regenerated by hydrolysis with water. In addition to being a raw material for varnish resins, indene is of interest on account of its pyrolysis to chrysene (60% yield).

The " dead oil " contains some naphthalene, which is a hydrocarbon of continually increasing importance, and is therefore recovered carefully from every fraction in which it occurs. Fortunately it is also the largest single constituent of coal tar, many tars containing as much as 10–11% of naphthalene. On standing, naphthalene crystallizes out of the dead oil, from which it is separated in a centrifuge. The middle (or carbolic) and heavy oils are the main sources of naphthalene, which crystallizes on settling the oils in shallow, rectangular pans. The oil is drained off from the bottom of the pans, and the crystalline residue is then " whizzed " in centrifuges to remove the adhering oil more thoroughly. The naphthalene, which may have a m.p. of 75° at this stage, is submitted to cold and hot pressing at 350 atmospheres pressure, when the m.p. rises to about 79°. Further purification is then effected by hot pressing, treatment with sulfuric acid and with alkali, and finally by distillation.

Naphthalene[15] is in enormous demand in the dyestuff industry for making the naphthols, naphthylamines and their sulfonic acids as intermediates for azo dyes, and for conversion into phthalic anhydride, which is an intermediate for anthraquinone derivatives. Large consumers of phthalic anhydride are the plastics and varnish industries, which therefore utilize a substantial proportion of the available naphthalene. A further use for the hydrocarbon is as moth-balls, although this is diminishing on account of its pronounced odor and the discovery of more efficient antiseptics and insecticides. Considerable quantities of naphthalene are also used for hydrogenation to tetrahydro- and decahydronaphthalene (tetralin and decalin), which are useful solvents.

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[15] For a comprehensive account of the isolation, purification and chemistry of naphthalene, see Rodd in Thorpe's Dictionary of Applied Chemistry, 4th ed., Vol. VIII, Longmans, London, 1947, p. 263.

When the dilute acid extracts of the light oils are made alkaline, a brown oil separates which contains aniline, pyridine, quinoline, isoquinoline, and other bases; pyridine bases are also obtained from the carbolic oils. Pure pyridine is usually not required in the dyestuff industry, since for use as a solvent, base and condensing agent, mixed pyridine bases are adequate. However, there is a growing demand for pure pyridine in the drug industry and for the manufacture of textile auxiliaries. Pyridine can be separated from the mixed bases by fractional distillation.

After removal of the naphthalene, phenols are extracted from the carbolic oils by means of warm dilute caustic soda solution.[16] Steam is blown through the alkaline extract to remove volatile hydrocarbons and bases; this "de-oiling" may be accomplished by running the extract down a packed column maintained at about 100° by closed and open steam coils. The residue, to which the caustic soda washings from the earlier operations are added, is allowed to flow down a packed column against an ascending stream of carbon dioxide. The phenolic layer liberated as a brown oil is washed and submitted to a series of fractional distillations under reduced pressure to yield crystalline phenol, a cresol fraction, and a heavy phenolic distillate mainly composed of the xylenols. In one procedure for the isolation of pure phenol, crude phenol is distilled, and the fraction between 175–210° which contains about 40% phenol is collected and cooled to 10°, when phenol containing some cresols crystallizes. The crystals are filtered on a centrifuge, mixed with about 15% of water and cooled to −10°, when phenol monohydrate, m.p. 17.2°, crystallizes. Distillation of the hydrated phenol, repeated in vacuum if necessary, finally gives pure phenol. Crude cresol contains 35–40% each of *o*-cresol (b.p. 191°) and of *m*-cresol (b.p. 202°), and about 25% of *p*-cresol (b.p. 201°). Although *o*-cresol differs only by 10° in b.p. from the *m*- and *p*-cresols, advances in the design of fractionating columns have enabled substantially pure *o*-cresol to be separated by fractional distillation. The *m*- and *p*-compounds are then separated by a chemical method due to Raschig;

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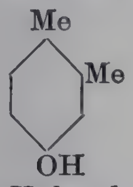
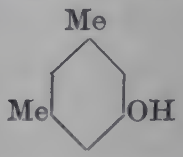
[16] In the "Phenosolvan process" phenol is extracted from gasworks ammoniacal liquor by means of butyl acetate or similar solvents; Lowenstein-Lom *et al.*, *Petroleum*, **10**, 82 (1947).

the mixture is sulfonated by means of concentrated sulfuric acid at 100° and separation is effected by taking advantage of the fact that the sulfonic acids desulfonate at different temperatures when superheated steam is blown into the acid solution. At 120–130° *m*-cresol comes over, followed by *p*-cresol at 150–160°. An alternative method is to separate the sulfonic acids by fractional crystallization prior to hydrolysis; *p*-cresolsulfonic acid is less soluble. *m*-Cresol can also be separated as the urea compound, which is subsequently hydrolyzed by water. Other methods for the separation of *m*- and *p*-cresol depend on the formation of addition compounds with oxalic acid,[17] fractional crystallization of phosphoric esters,[18] and alkylation with an olefin.[19] The xylenols which have been commercially isolated from coal tar are the *o*-4-, *m*-4-, *p*-2- and *m*-5-compounds. The methods of separation depend on differential solubilities in 25% caustic soda solution and on sulfonation-desulfonation.[20] The *m*-5-isomer is the most abundant and is also the most valuable because of its having the *para* position and both the positions *ortho* to the hydroxyl group free for the production of plastics by formaldehyde condensation. The *o*-4-compound is useful for varnish resins.



o-4-Xylenol



m-5-Xylenol

The cresols and xylenols have only a limited use in the dyestuff industry, and phenol can be conveniently made by synthesis from benzene. The entire phenolic oil as well as mixtures of phenols from which the individually valuable constituents have been separated have a ready market as disinfectants. The cresols are more powerful antiseptics and bactericides than pure phenol; and crude cresol fractions are marketed in various forms for disinfectant purposes, e.g., as solutions of the alkali salt (the solveol type) and soap emulsions of the free phenols (the lysol type). More potent disinfectants and antiseptics are obtained by chlorinating the cresols, especially *m*-cresol and *m*-5-xylenol (3,5-xylenol). Another use for the cresylic acids, especially if the xylenol content is high, is as a wetting agent in mercerizing cotton.

The heavy oils freed from naphthalene are usually distilled to give three fractions: a small first fraction of phenols, a valuable second fraction containing methylnaphthalenes and acenaphthene, which crystallizes on cooling, and a residue which is added to the anthracene oils. From a cut of narrow b.p. range acenaphthene crystallizes readily, but contaminated with fluorene, and is purified by recrystallization from solvents such as alcohol or petroleum naphtha. The fraction boiling at about 240-255° can be worked up for indole, α- and β-methylnaphthalenes.[21] From the 260–270° fraction of the heavy oils, seven of the ten possible dimethylnaphthalenes have been isolated (see Table I). The 280–290° fraction deposits a large amount of mixed crystals on cooling, consisting chiefly of acenaphthene, diphenylene oxide and fluorene. Pure diphenylene oxide[22] melts at 82.8–83°; diphenylene oxide isolated from coal tar is liable to be contaminated with acenaphthene or fluorene, as much as 20% of the latter changing the m.p. but little from 82.8° From the residual oil 2,3,6- and 1,3,7-trimethylnaphthalenes have been isolated. 3-Methylindole (skatole) has been isolated by a technically feasible process from carefully fractionated indole oil boiling mostly between 267° and 270°.[10] The desired compound occurs together with the 2-, 5- and 7-isomers, and separation of skatole is based on the fact that it is the only one of the four compounds which does not form a carboxylic acid when the sodium derivative is treated with carbon dioxide.

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[17] Engel, USP 2,095,801; Gould, USP 2,099,109.

[18] Kotake, JP 133,250.

[19] Stevens, *Ind. Eng. Chem.* **35,** 655 (1943).

[20] Brückner, *Z. angew. Chem.* **41,** 1043, 1062 (1928); Kester, *Ind. Eng. Chem.* **24,** 770 (1932). See also Cislak and Otto, USP 2,456,581-2.

The heavy oils as such have many uses, so that fractionation is practised only in accordance with the demand for acenaphthene and other constituents. An important use of the heavy oils is for stripping aromatic hydrocarbons from coal gas, and other uses are in the treatment of timber against dry-rot, for the production of lampblack, and as fuel.

The anthracene oils contain phenols, naphthalene, diphenyl, phenanthrene, carbazole, acridine, and only about 2–4% of anthracene. The isolation of *anthracene* of adequate purity for oxidation to anthraquinone is tedious, but is still practised in Europe; in the United States anthraquinone is made solely by the phthalic anhydride route. One reason for working up the anthracene oils is the increasing demand for carbazole which is the raw material for a largely used dye (Hydron Blue), a synthetic resin with valuable electrical properties (polymerized *N*-vinylcarbazole; Luvican, IG),[23] and tetranitrocarbazole, which is an insecticide. Carbazole, however, can also be produced synthetically. If crude anthracene is not exploited by refinement, it is used for carbon black manufacture. The oil on cooling forms a green fluorescent mass of the consistency of butter, and separation in a suction filter gives a residue with about 15% anthracene content.

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[21] The isolation of α- and β-methylnaphthalenes on a large scale by a process of sulfonation and desulfonation has been described by Coulson, *J. Soc. Chem. Ind.* **60,** 123 (1941); **62,** 177 (1943).

[22] Williams, *Nature* **162,** 925 (1948).

[10] See p. 34.

[23] For the preparation of *N*-vinylcarbazole and its polymerization see *BIOS* **746.**

Cold and hot pressing in a hydraulic press at 200–300 atmospheres raises the percentage to about 40. Successive washing with solvent naphtha and pyridine (or other suitable solvents, such as acetone and high-boiling phenols, in which the impurities are more soluble than anthracene) yields a product which mainly consists of anthracene (about 80%) and carbazole. The older method of removing the carbazole was to heat the anthracene-carbazole mixture with potassium hydroxide at about 230°, when potassium carbazole separates as the lower layer.[24] The usual method at the present time is to dissolve the carbazole with pyridine. Crude anthracene contaminated with 20–25% of carbazole can be raised to 94–95% purity by two extractions with hot pyridine bases (b.p. 130–150°) at about 90°, cooling to 20° and filtering. A final crystallization from pyridine[24a] raises the purity to 97%. The anthracene is then dried under a good vacuum, and a current of nitrogen is passed through the dryer before it is opened, since explosions can otherwise occur.[25] By sublimation of this anthracene, 99.9% purity can be achieved. In a continuous process[26] for separating carbazole from anthracene, benzene percolates through crude anthracene, the solution is washed with 80–86% sulfuric acid at 20–30°, carbazole sulfate separates from the acid at a concentration of 2–5% and is filtered off, and nearly pure anthracene is recovered from the benzene which is then returned to the process. Anthracene of 90–95% purity may be sublimed in superheated steam to yield a very finely divided material suitable for oxidation to anthraquinone.

Phenanthrene is present in the washings from crude anthracene, being more soluble in the common organic solvents than anthracene. Pure phenanthrene is difficult to prepare because it forms mixed crystals with anthracene, fluorene, and carbazole; diphenylene oxide is also present. Laborious procedures have been suggested, based on selective solubilities, treatment with metallic sodium,[27] and the readier oxidation of anthracene to the quinone. Phenanthraquinone is useful in the laboratory for the characterization of *o*-diamines when easily crystallizable quinoxalines are formed; but phenanthrene and phenanthraquinone are of little interest in the manufacture of dyes.

Carbazole can be recovered from the pyridine washings of anthracene, and purified by repeated crystallization from solvent naphtha. One process,[25] which gives 97–98% carbazole in a yield of about 74% of the carbazole contained in the anthracene residues, is to distil the pyridine extracts from the purification of anthracene under reduced pressure with dry steam until all traces of pyridine are removed. The dry residue is heated with chlorobenzene at 140° with mechanical agitation, cooled to 40°, and stirring stopped. The heavier carbazole settles quickly to the bottom, and the upper layer of liquid and suspended impurities is siphoned off. The treatment is repeated, and the adhering solvent finally removed from the carbazole in a vacuum dryer. Carbazole in coal tar fractions may be estimated as the picrate, or by separation as *N*-nitrosocarbazole, decomposition of the latter by heating with ferrous sulfate solution and measurement of the nitrous gases evolved.[28]

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[24] The fusion process for separating carbazole from anthracene cake has been improved by a three-stage process, Koppers Co., USP 2,419,969; for a process using maleic anhydride see Insinger and Koppers Co., USP 2,440,688.

[24a] Hatton and May, BP 611,554, suggest the use of cyclohexylamine.

[25] *BIOS* 939.

[26] Weinmayr and du Pont, USP 2,242,842.

[27] Jeanes and Adams, *JACS* 59, 2608 (1937).

Pyrene and Chrysene.[29] Chrysene, fluorene, and fluoranthene, besides pyrene which appears to be well established as a raw material for dyes, are being increasingly investigated as possible sources for the preparation of vat dyes.[30] Pyrene and chrysene were both discovered in coal tar by Laurent (1837), and chrysene was so named because of its golden yellow color. Liebermann (1871) later prepared chrysene as a colorless substance, the main colored impurity being naphthacene which can be separated by chromatography.[31] Technical chrysene from coal tar also contains as much as 1.4% of sulfur compounds, which can be removed by a treatment with metallic sodium.[32] From a coal-tar fraction boiling at 370–390°, pyrene and fluoranthene can be isolated;[33] the separation is based on the latter forming with metallic sodium a sodium derivative which is hydrolyzed and distilled to form tetrahydrofluoranthene, from which fluoranthene is recovered by selenium dehydrogenation. Studying the chromatographic adsorption of aromatic compounds on Japanese acid earth, Yukawa[34] has separated anthracene, carbazole, naphthacene, 1,2,5,6-dibenzanthracene, chrysene, fluorene, and phenanthrene from anthracene cake.

The pitch remaining in the still at the end of the primary distillation of tar was until recently used only for road-making and similar purposes. Pitch (Chart 1) is a source of pyrene and chrysene,[35] which may be isolated by steam distillation, followed by fractional distillation and crystallization from solvent naphtha.[36] The residual hard pitch can be carbonized in pitch-coking ovens to yield gas, fuel oil, and coke.

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[28] *BIOS* **1363.** See also Coulson and Biddiscombe, *Analyst* **74**, 46 (1949).

[29] See also Chapter XXXII.

[30] German practice in the production and utilization of high boiling coal-tar chemicals is reported in *BIOS* **1783.**

[31] Winterstein, Schon, and Vetter, *Z. physiol. Chem.* **230**, 158 (1934). See also Wieland and Müller, *Ann.* **564**, 199 (1949).

[32] von Braun and Irmisch, *Ber.* **65**, 883 (1932).

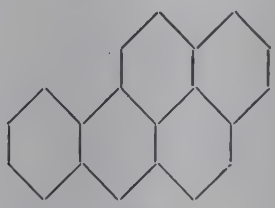
[33] Kruber, *Ber.* **64**, 84 (1931); see also Coulson, *Chemistry & Industry* **60**, 699 (1941).

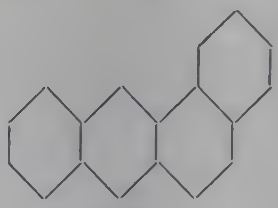
[34] *J. Chem. Soc. Japan*, **63**, 150 (1942).

[35] IG, DRP 654,082; 654,791.

Pyrene can be isolated economically by the distillation of a fraction of hydrogenated coals or coal tars;[37] mixed trichloro- and tetrachloropyrenes can be obtained by chlorinating pyrene-containing fractions of coal tar or hydrogenated coal in a solvent such as nitrobenzene.[38]

The occurrence of skin cancer as an occupational disease among workers in coal-tar plants has been traced to some of the polynuclear hydrocarbon constituents. Using fluorescence spectroscopy for tracing the progress of the concentration, Cook [39] isolated 7 g. of pure 2,3-benzpyrene (I), a very potent carcinogen, from two tons of pitch. Employing chromatographic technique Winterstein and Vetter[40] were able to isolate 2.5 g. of the hydrocarbon from 3.5 kg. of a coal-tar fraction boiling above 450°. 1,2-Benzanthracene (II), which also occurs in coal tar, has little or no carcinogenic activity, although it is the parent hydrocarbon from which most of the potent carcinogens are derived.


(I)


(II)

LOW TEMPERATURE CARBONIZATION[41]

Differences in the composition of coal tar from different coals become less and less as the temperature of carbonization is increased, since the pyrolysis at high temperatures tends to yield nearly the same products. At lower temperatures less pitch is formed. The yield of tar is higher (18–20 gallons as against 8–12 gallons per ton of coal in high temperature carbonization), and the composition of the tar depends much more on both the quality of the coal and the carbonization temperature. Carbonization at about 600° yields a high-grade tar, together with smokeless domestic fuel, and the process is particularly useful for coal fines rich in volatile matter. An important product of low-temperature carbonization is the high-octane aviation gasoline obtained by stripping the gas, corresponding to the recovery of benzene and toluene by scrubbing coke-oven gas with heavy oils. Low temperature tar (sp. gr. about 1) contains very little benzene, toluene, naphthalene, or anthracene, but it contains 15–20% of phenols,[42] the remainder being alkanes, alkenes, naphthenes and resinoids. Alkylation of aromatic systems is a characteristic reaction during low temperature carbonization, and while the tar contains phenol, pyridine, and anthracene in small amounts, the *C*-methyl derivatives are the major constituents among the aromatics.[43] As a raw material for the dyestuff industry, low-temperature tar is of no interest, and its use is chiefly as fuel and for disinfectant purposes.

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[36] See also Curtis, USP 2,419,011.

[37] IG, BP 435,254.

[38] Carter and ICI, BP 584,770.

[39] Cook, Hewett, and Hieger, *JCS* 395 (**1933**); see also Berenblum, *Nature* **156,** 601 (1945).

[40] *Z. physiol. Chem.* **230,** 169 (1934).

[41] For an account of the development of liquid products from low temperature carbonization, see Bristow, *J. Inst. Fuel* **20,** 109 (1947).

Aromatic Hydrocarbons from Petroleum

Aromatic hydrocarbons have become available from petroleum in recent years. Most petroleums contain some aromatic constituents; Borneo crudes for instance contain as much as 30–40% and were exploited for toluene production in the first world war.[44] When the high-boiling fractions in the distillation of petroleum are submitted to high temperatures and pressures, they break down or crack to smaller molecules, and under suitable conditions dehydrogenation resulting in the formation of a large proportion of benzenoid hydrocarbons takes place. The products have the advantage that no phenols, bases, or sulfur compounds are present. Normally, the essential object of petroleum cracking processes, practised on a vast scale, is to produce high grade gasolines, but benzene and toluene can be fractionated if desired. The availability of benzene and toluene from coal tar depends on the extent of by-product coking, and an independent source of these important primary materials for the organic chemical industries is very valuable, especially in war time when the demand for chemicals derived from the aromatic hydrocarbons rises steeply. The bulk of the toluene for nitration in the United States during the second world war came from the petroleum industry. In 1925 petroleum derivatives constituted less than 0.1% of the organic chemicals manufactured in the United States, the products being isopropyl alcohol and a few chlorinated hydrocarbons. At the present time 28% of the total volume of organic chemicals is derived from petroleum or natural gas. Hydrocarbons available from petroleum cover a wide range starting from methane. By cracking, hydrogenation, alkylation, and polymerization reactions, various new carbon skeletons may be prepared. Petroleum crudes also contain sulfur-, nitrogen-, and oxygen-containing compounds; and phenols can be isolated. The production of cresols from petroleum in 1945 was over 10 million pounds, about 35% of the total production of the United States.[45]

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[42] Low temperature carbonization in Germany and the recovery of phenols, *e.g.*, by the Phenosolvan process, is described in *BIOS* **938**.

[43] Morgan and Pratt, British Chemical Industry, Arnold, London, 1938, p. 224.

[44] For a survey of the chemical refining of aromatic hydrocarbons from petroleum, see Brandt, Lee, and Wadsworth, *Ind. Eng. Chem.* **39,** 1011 (1947); for an account of the production of aromatic hydrocarbons for aviation fuels by solvent extraction of petroleum fractions, see Moy, *Ind. Chemist* **24,** 433 (1948). See also Weiss, *Chem Eng. News* **27,** 972 (1949).

The production of aromatic hydrocarbons from the naphtha and naphthene (cycloparaffin) fractions of petroleum involves a complex mechanism of degradation to smaller molecules, polymerization and dehydrogenation; the technical processes are many, and vary in the nature of the charging stock, temperature, pressure and use of catalysts. In the cracking process, known as reforming, a high pressure and a very brief time of treatment of a few seconds are employed, catalysts such as silica-alumina-manganese dioxide (Houdry catalyst) and chromic oxide being used to increase the formation of aromatics. When heavy naphtha and naphthene fractions are treated with hydrogen at temperatures of the order of 300° under certain conditions, the octane number rises and aromatization takes place with the formation of benzene, toluene, and xylenes in varying proportions. Toluene is obtained in high yield from a naphthene fraction boiling at 65–130° or other types of hydrocarbon oils boiling at 65–290° by treatment with hydrogen at a temperature in excess of 260° in presence of a dehydrogenation catalyst such as alumina containing 1-20% of an oxide of molybdenum, chromium, cobalt, nickel, titanium, or vanadium; the aromatics are extracted with liquid sulfur dioxide at −34 to −55°.[46] This "hydroforming" process was developed in the United States during the war for increasing the supply of toluene, other fractions being separated and used in high grade gasolines. The DHD (Dehydrierung-Hoch-Druck) process of the IG at Leuna for the catalytic dehydrogenation of naphthenes to aromatic hydrocarbons, using 10% molybdic oxide on alumina as catalyst, has been described.[47] In the Catarole process, catalysts are used which enable an almost entirely aromatic product to be recovered.[48] In the plant operated by Petrochemicals in England, an output of 3000–5500 tons each of pure benzene and pure toluene, 1000–1500 tons of naphthalene, and of a number of other aromatics is expected.

Methods for aromatizing natural and cracked gases have been successfully developed, and a more recent innovation is the use of individual hydrocarbons. Thus *n*-heptane has been converted into toluene in yields of about 90% by dehydrogenation over oxides of aluminum, chromium and molybdenum. Toluene in a yield of 51–57% has been obtained in a British process using *n*-heptane derived from Fischer-Tropsch oil and a chromic acid catalyst supported on active alumina.[49]

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[45] Egloff, *Ind. Chemist* **23**, 616 (1947).

[46] Standard Oil Co., BP 577,171; 577,282.

[47] *CIOS* Item **30**, File XXXII–107.

[48] Madaras, *Dyer* **100**, 361 (1948).

Whatever process of aromatization is employed, the conversion is never complete, and the aromatic hydrocarbons have to be separated from the nonaromatics, in addition to the isolation of the individual constituents. Fractional distillation, azeotropic distillation[50] using methanol, methyl ethyl ketone[51] or phenol as entrainer, and chemical refining are all employed.[44] A combination of fractional and azeotropic distillation and acid treatment may be used.[52] Aromatics can be separated as a complex with liquid hydrogen fluoride containing boron trifluoride.[53] Liquid sulfur dioxide is a good solvent for separating toluene from paraffin hydrocarbons.[54]

TESTS AND STANDARDS OF PURITY[55]

Benzene and **toluene** of adequate purity as primary materials for dye manufacture are usually described as being of nitratable quality, since nitration in particular requires the use of these hydrocarbons in a state of carefully specified purity. British Standard Specification[56] for "pure benzole" lays down the following properties: color not darker than a solution of 0.8 cc. of 0.1N potassium dichromate and 12 cc. of 0.1N cobalt sulfate made up to one liter with distilled water; sp. gr. at 15.5° between 0.880 and 0.885; free from undissolved water and other separated impurities; distillation range between 79.5° and 80.5°; no darkening or turbidity on shaking with 95% sulfuric acid; not more than 0.2% of total sulfur and not more than 0.1% of sulfur as carbon disulfide; no corrosive sulfur, as indicated by not more than a slight discoloration to a copper strip; negative reaction of hydrogen sulfide and mercaptans; neutrality to a mixed indicator of Bromocresol Green and Alizarine Red S; and less than 10 mg. of residue from 100 cc. on evaporation. The total sulfur is determined by diluting a sample with alcohol, burning it in a lamp, drawing the combustion products through neutral hydrogen peroxide solution, and titrating the resulting acidity with sodium carbonate solution. Carbon disulfide is determined by treatment with alcoholic potassium hydroxide and titration of the potassium xanthate with iodine to form dixanthogen and potassium iodide. Thiophene estimation is based on the formation

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[49] Cawley *et al.*, *J. Inst. Petroleum* **32,** 660 (1946).

[50] Reed and Holt, USP 2,413,245.

[51] Lake, *Trans. Am. Inst. Chem. Eng.* **41,** 327 (1945).

[44] See p. 43.

[52] Waldron, USP 2,419,521.

[53] Burk and Standard Oil Co., USP 2,343,744.

[54] Kimball, USP 2,410,166.

[55] Standard Methods for Testing Tar and its Products, Standardization of Tar Products Test Committee, London, 1938.

[56] British Standard Specification No. 135 (1939).

$$2KS\text{–}CS\text{–}OEt + I_2 \longrightarrow 2KI + EtO\text{–}CS\text{–}S\text{–}S\text{–}CS\text{–}OEt$$

of an additive compound with basic mercuric sulfate, the method giving accurate results only in the complete absence of unsaturated hydrocarbons. The well-known indophenin reaction (an intense blue color with isatin and sulfuric acid) is a sensitive qualitative test for thiophene.

The specification[57] for "pure toluol for nitration" is similar, making the relevant changes in the physical properties, but the limit for total sulfur is 0.1%.

***m*-Xylene** in xylol is determined[58] by treatment with nitric acid under controlled conditions, crystallizing the trinitro-*m*-xylene from acetone and weighing, allowance being made for the material remaining in solution.

Naphthalene is volatile even at room temperature, and a simple test for purity is to volatilize a weighed amount in air; the substance must remain colorless throughout and finally leave no residue. Commercial naphthalene is practically pure. The main test is the crystallizing point determined in a standard apparatus in which molten naphthalene at 85° is cooled and the temperature noted at half-minute intervals; the crystallizing point corresponds to the first five consecutive readings during which the temperature remains constant within 0.05°. It is important that no paraffin or olefin hydrocarbons are present as indicated by testing with concentrated or 98–99% sulfuric acid. Qualitative tests for pyridine bases and phenols must be negative.

Anthracene (lustrous plates with a violet-blue fluorescence in both the crystalline and dissolved states) for use in the manufacture of anthraquinone does not need to be chemically pure, and 90% anthracene can be utilized, although the purer the sample, the easier it is to work up the anthraquinone after oxidation. Commercial qualities may contain as little as 30% anthracene, and a method of estimation is therefore necessary. The standard procedure[59] is based on oxidation of the sample by means of chromic anhydride in glacial acetic acid, dilution, filtration of the precipitate of crude anthraquinone, removal of impurities by successive treatment with boiling 1% caustic soda solution and ten times its weight of 10% fuming sulfuric acid at 100°, washing, drying and weighing the product; and finally weighing the residue after sublimation by heating over a low flame, the difference giving the weight of pure anthraquinone. Anthracene can also be estimated by condensation with maleic anhydride, followed by titration of the excess reagent. For dyestuff manufacture anthracene must be substantially free from carbazole; the carbazole content (up to 6%) can be estimated by a colorimetric method based on the formation of a blue condensation product with salicylaldehyde in glacial acetic acid solution in presence of sulfuric acid.[60]

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[57] British Standard Specification No. 805 (1939).

[58] Reichel, *Chem. Ztg.* **55, 744** (1931).

[59] Rhodes, Nichols, and Morse, *Ind Eng. Chem.* **17,** 839 (1925).

Phenol rapidly turns pink in color on exposure to light and air. The chief physical test is the crystallizing point. At 16° phenol dissolves in 15 parts of water, and the solubility rises rapidly with temperature, until at 84° it is completely miscible with water. At room temperature, phenol dissolves a little water which is sufficient to liquefy the crystals, so that the solid crystalline character of a sample is a good indication of its purity. A method of estimation is to dissolve in caustic soda solution, add standard iodine solution when tri-iodophenol separates, and titrate the excess of iodine with thiosulfate. Solubility in aqueous caustic soda with no smell of naphthalene or other hydrocarbons on heating is the rough test of purity employed in works practice.

In phenol-cresol mixtures containing 20% or more of phenol, phenol can be estimated by observing the crystallizing point and comparing with a table of crystallizing points of known mixtures.

***m*-Cresol** in a mixture of cresols is estimated (Raschig, 1900) by treatment with concentrated sulfuric acid and 62% nitric acid at 100°, when *m*-cresol forms the trinitro compound which is collected and weighed, whereas the isomers are oxidized to oxalic acid. *o*-Cresol present to the extent of 40% or more in a phenol-cresol mixture can be estimated by determining the freezing point of a mixture of the sample with cineol and comparing with a standard freezing point curve.[61] Phenols and cresols in admixture can be estimated by means of the ultraviolet absorption spectra of the vapors.[62]

Carbazole (colorless plates) can be estimated by bromination in acetic acid to the tetrabromo derivative. Characteristic color tests for carbazole are based on the reaction with isatin in sulfuric acid which results in a deep blue color, and on the reaction with oxalic acid at 200° to form "carbazole blue."

SYNTHESIS OF PRIMARY MATERIALS

Many of the compounds occurring in coal tar are more commonly made by synthesis starting from the simple hydrocarbons such as benzene, toluene, and naphthalene, so that the term "coal-tar primaries" may be restricted in practice to those substances which are isolated directly from coal tar as the normal commercial source. Phenol is a primary as well as an intermediate since coal-tar phenol and synthetic phenol from benzene are both commercial products. Several of the other coal-tar primaries can be synthesized by technically feasible methods, starting from other coal-tar primaries or from the aromatic hydrocarbons obtained by the aromatization of petroleum fractions. These interconversions are of interest in some cases for the light they throw on the reactions which take place during the carbonization of coal and distillation of the tar; from the commercial point of view also they are significant, since the demand for individual coal-tar products is liable to fluctuate, some of the reasons being the discovery of new uses, the replacement of one primary by another in the manufacture of a known product, and the special requirements of war. A few examples of such syntheses may therefore be cited.

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[60] Strafford and Stubbings, *Rec. trav. chim.* **67**, 918 (1948).

[61] Potter and Williams, *J. Soc. Chem. Ind.* **51**, 59T (1932). For a review of methods of analysis of cresols, see Mlle. Sansin, *Ann. chim. anal.* (iii), **21**, 89 (1939).

[62] Robertson, Ginsburg, and Matsen, *Ind. Eng. Chem., Anal. Ed.* **18**, 746 (1946).

Dibenzyl is obtained in 90–100% yield by the interaction of benzene with ethylene dichloride in presence of aluminium chloride and aluminium;[63] and dibenzyl can be converted[64] into a mixture of toluene and ethylbenzene by treatment with hydrogen in presence of a catalyst (e.g., zinc chloride on alumina) at 400° under a pressure of 100 kg. per sq. cm. A mixture of benzene with 8% of dimethyl ether passed over a phosphate catalyst at 400° and 200 atmospheres pressure gives a mixture of hydrocarbons containing 18% toluene, 4% xylenes and 4% polymethylbenzenes.[65] Toluene may be produced by the pyrolysis of xylene or xylene-rich fractions at 600–1000° in presence of hydrogen or hydrogen-rich gases.[66] An interesting process for the production of toluene is from phthalic acid or anhydride by catalytic hydrogenation at about 400° over vanadium or molybdenum oxides at pressures of 200 atmospheres.[67] Benzene, toluene, and *o*-xylene are produced by the reaction of naphthalene with hydrogen at 200 atmospheres pressure in presence of basic stannic acetate.[68] Mesitylene can be synthesized by the action of sulfuric acid on acetone;[69] or the condensation of acetone in presence of silica gel or alumina;[70] or by the methylation of benzene, toluene, or *m*-xylene.[71] The methyl groups in the xylenes migrate under the influence of aluminium chloride.[72]

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[63] van Schaack, Jr., USP 2,344,188.

[64] Schmerling and Universal Oil Prods. Co., USP 2,338,973.

[65] Gas Light and Coke Co., BP 577,314.

[66] Stanier, Davis, and South Metropolitan Gas Co., BP 569,035.

[67] Griffith and Gas Light and Coke Co., BP 577,816.

[68] Griffith, Plant and Gas Light and Coke Co., BP 577,818.

[69] Kane (1838); Adams and Hufferd, *OSCV* I, p. 341.

[70] Mitchell and Reid, *JACS* **53**, 330 (1931); IG, DRP 597,059.

[71] Norris *et al.*, *JACS* **62**, 874 (1940) and earlier papers.

[72] Norris and Vaala, *JACS* **61**, 2131 (1939).

Anthracene can be synthesized from toluene in a yield of 35% by passage over an alumina-chromic oxide catalyst at 550°, and recycling.[73]

IG attempted during the war to manufacture carbazole synthetically, in view of the restricted supplies of anthracene oil which was also needed for carbon black.[74] Among the reactions which were studied, the Tauber synthesis from *o*-nitrochlorobenzene was regarded as the most promising; self-condensation in presence of copper gave *o,o'*-dinitrodiphenyl, which was reduced to the diamine and cyclized to carbazole by heating with 63% phosphoric acid. The method of Morgan and Walls,[75] which is a pyrolysis of *o*-xenylamine at 500–600° in presence of vanadium pentoxide or other oxidation catalyst, has found industrial application; diphenyl from the pyrolysis of benzene has become readily available, and *o*-xenylamine can be prepared in good yield from diphenyl.

Pyrolysis of indene in presence of zinc or magnesium oxide at about 700° yields chrysene in good yield.[76]

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[73] Mattox, Grosse and Universal Oil Products Co., USP 2,180,814.

[74] *CIOS* Item No. **22**, File No. XXVI–11.

[75] Morgan and Walls, *J. Soc. Chem. Ind.* **57**, 358 (1938); Conover and Monsanto Chemical Co., USP 2,479,211; 2,481,292.

[76] Spilker, *Ber.* **26**, 1538 (1893); Wulff and Treppenhauer, USP 2,056,915.

CHAPTER III

INTERMEDIATES

Benzene, toluene, naphthalene, anthracene, and the other coal-tar primaries are converted into dyes *via* various intermediate products,[1-13] prepared by a series of reactions such as sulfonation, alkali fusion, nitration and reduction, chlorination, oxidation, and condensation, which may be called the unit processes of organic synthesis.[4, 14] By these methods, sulfonic, hydroxyl, alkoxyl, amino, and other groups are introduced into the parent hydrocarbons ; or in a few cases, notably the preparation of anthraquinone and its derivatives from naphthalene through phthalic anhydride, more complex ring systems are synthesized. The chemistry of the dyestuff intermediates covers nearly the whole of aromatic chemistry,[15] and many of them are of interest and use in fields outside the synthesis of dyes.

Because of the wide variety of the intermediate products and of the reactions involved, and for other reasons such as the comparatively large size of the smallest economic units, the manufacture of intermediates often presents more difficulties than the conversion of intermediates into dyes. It is therefore not unusual for producers with limited resources to undertake the manufacture of dyes using intermediates obtained elsewhere. It is obvious at the same time that a national dyestuff industry has to be based on a cheap and adequate domestic supply of intermediates. The major color-manufacturing countries have consequently become more or less self-sufficient in intermediates, and the experience gained as a result has had

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[1] Cain, The Manufacture of Intermediate Products for Dyes, 2nd ed., Macmillan, London, 1919.

[2] Davidson, Intermediates for Dyestuffs, Benn, London, 1926.

[3] Fierz-David and Blangey, Grundlegende Operationen der Farbenchemie, 5th ed., Springer, Wien, 1943; lithoprinted by Edwards, Ann Arbor.

[4] Groggins, Unit Processes in Organic Synthesis, 3rd ed., McGraw-Hill, New York, 1947. For a recent review, see *Ind. Eng. Chem.* **41**, 1821 (1949).

[5] Rodd has given an exhaustive account of the chemistry of naphthalene intermediates for dyes in Thorpe's Dictionary of Applied Chemistry, Vol. VIII, Longmans, London, p. 263–438.

[6-12] *BIOS*: (6) **986**; (7) **987**; (8) **1149**; (9) **1152**; (10) **1153**; (11) **1484**; (12) **1493**

[13] *BIOS* **1157** gives notes on numerous dye intermediates, but the details are only available in documents listed in the Appendices and filed in *BIOS* Information Section.

[14] Recent reviews in *Ind. Eng. Chem.* **40**, 1556-1684 (1948).

[15] See, therefore, treatises on organic chemistry, besides the special references which are cited.

important developments in other branches of the organic chemical industry. Instances in point are catalytic reductions and oxidations, high-pressure reactions, and the design, fabrication, and operation of the special plant required for these purposes.

Intermediates of general interest in the dyestuff industry, in the sense that each of them is used in the preparation of a number of dyes, are described in this chapter. Intermediates whose uses are limited to the production of individual dyes (e.g., phenylglycine for the production of indigo) or of dyes of the same type (e.g., phenylhydrazine and its derivatives for the production of pyrazolones, and benzanthrone for dibenzanthrone and similar vat dyes) are more conveniently treated together with the relevant dyes.

SULFONATION

Aromatic compounds have the characteristic property of reacting with concentrated or fuming sulfuric acid to form sulfonic acids ($Ar—H + H_2SO_4 \longrightarrow Ar—SO_3H + H_2O$), water being eliminated.[16] The readiness with which sulfonation takes place, however, varies considerably. Benzene and toluene can be sulfonated in the cold, whereas anthraquinone requires fuming sulfuric acid and high temperatures. With a given substance, sulfonation can usually be effected by heating with sulfuric acid[17] or by means of oleum at a lower temperature, so that oleum is convenient to use in the case of compounds which are liable to decompose. When it becomes necessary to use oleum at a high temperature, it is difficult to limit the reaction to the production of the monosulfonic acid. During the sulfonation of a polyalkylbenzene, a polyhalogenated benzene, or a halogenated polyalkylbenzene, migration of an alkyl group or of a halogen atom can occur.[18] Aromatic hydrocarbons may be sulfonated in nearly quantitative yields by means of an equivalent quantity of sulfur trioxide,[19, 20] using

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[16] The direct sulfonation of aromatic hydrocarbons and their halogen derivatives has been reviewed by Suter and Weston, Organic Reactions, III, Wiley, New York, 1946, p. 141-197. The sulfonation of aromatic compounds in nitrobenzene solution by sulfuric acid and by sulfur trioxide has been studied by Hinshelwood, *JCS* 1065 (**1948**) and earlier papers, with reference to the kinetics of the reactions. The factors affecting the yield and course of sulfonations, and methods for the quantitative control of sulfonation processes have been reviewed by Simpson and Olsen, *Ind. Eng. Chem.* **29**, 1350 (1937).

[17] Sulfuric acid in this chapter refers to the ordinary concentrated acid of about 98% strength.

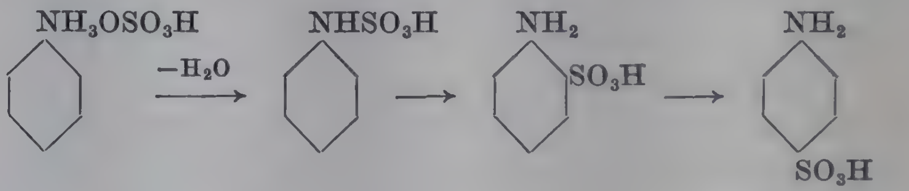
[18] The Jacobsen reaction has been reviewed by Smith, Organic Reactions, I, Wiley, New York, 1942, p. 370-384.

[19] Leiserson, Bost, and LeBaron, *Ind. Eng. Chem.* **40**, 508 (1948); du Pont, BP 439,056; 439,093.

[20] Stabilized sulfur trioxide ("Sulfan"; General Chemical Co.) is now commercially available in the United States.

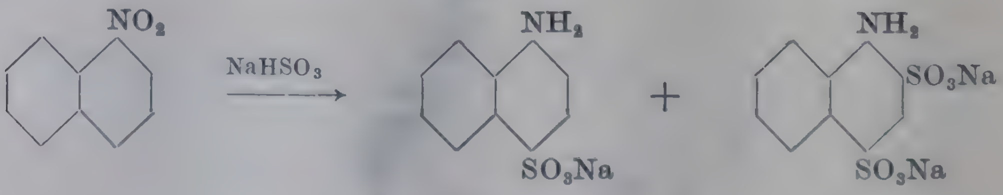
NOLOGICAL

sulfur dioxide as solvent, catalyst, and refrigerant. Vanadium pentoxide and iodine are sulfonation catalysts; boron trifluoride is a promoter for sulfonations and nitrations.[21] The sulfonation of anthraquinone by means of fuming sulfuric acid normally leads to the β-acids, but in the presence of mercuric oxide the sulfonic groups enter the α-positions. Other sulfonating agents which may be employed are a mixture of sulfuric acid and sodium bisulfate, chlorosulfonic acid which is more useful for the preparation of sulfonyl chlorides, and sulfamic acid. Dioxane and sulfur trioxide form a crystalline addition product which is a sulfonating agent, useful for sulfonating aromatic compounds and for preparing alkyl sulfuric esters.[22] A sodium sulfonate group can be introduced by the replacement of a chlorine atom by heating with aqueous sodium sulfite under pressure (*p*-chlorobenzaldehyde ⟶ benzaldehyde-*p*-sodium sulfonate; 1,4-dichloroanthraquinone ⟶ disodium anthraquinone-1,4-disulfonate).[23] Sulfanilic and naphthionic acids, which are important intermediates, are prepared by the "baking" process, which consists in heating the acid sulfate of an amine at about 180°; an intramolecular change occurs with the formation



Sulfanilic acid

of the amine sulfonic acid in nearly quantitative yield. The evidence for the indicated mechanism (Bamberger, 1897) is by no means conclusive. The action of sodium bisulfite on α-nitronaphthalene gives sodium naphthionate, together with smaller amounts of α-naphthylamine and the sodium salt of the 2,4-disulfonic acid (Piria, 1851).



Sodium naphthionate

The reaction proceeds through α-nitrosonaphthalene, α-naphthylhydroxylamine and sodium α-naphthylsulfamate.[24] The interaction of

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[21] Thomas, Anzilotti, and Hennion, *Ind. Eng. Chem.* **32**, 408 (1940).

[22] Suter, Evans, and Kiefer, *JACS* **60**, 538 (1938).

[23] Kozlov, *J. Gen. Chem. U.S.S.R.* **17**, 289 (1947).

[24] Sprung *et al.*, *JACS* **53**, 1432, 1443 (1931); **58**, 225 (1936); Goldblum and Montonna, *J. Org. Chem.* **13**, 179 (1948).

m-dinitrobenzene and sodium sulfite gives the sodium salt of 3-nitroaniline-4-sulfonic acid. A similar reaction of technical importance in the anthraquinone series is the conversion of 1,5-dinitro-4,8-dihydroxyanthraquinone by boiling sodium bisulfite solution to the disodium salt of 1,5-diamino-4,8-dihydroxyanthraquinone-3,7-disulfonic acid (Alizarin Saphirol B).[25] Quinizarin (1,4-dihydroxyanthraquinone) gives the sodium salt of the 2-sulfonic acid on treatment with boiling sodium sulfite solution.

Technical sulfonations are usually carried out by agitation of the substance with sulfuric acid in a cast iron or mild steel pot, which is provided with a jacket for heating or cooling, an agitator, and a cover fitted with a manhole, a thermometer pocket, and a bottom discharge or a pipe for blowing out the charge at the end of the process. The progress of the reaction is followed by examining the solubility in water and aqueous alkali. The general procedure for working up the product is to neutralize with lime, filter off the calcium sulfate, add the calculated amount of sodium carbonate to the filtrate, filter off calcium carbonate, and concentrate the filtrate until the sodium sulfonate crystallizes or use the solution directly for later processes. In some cases the sulfonic acid can be salted out of the sulfonation mixture as the sodium salt by the addition of common salt.

Benzenesulfonic acid ($C_6H_5SO_3H$, $1{\cdot}5H_2O$; colorless plates, m.p. 43-44° ; anhydrous, m.p. 65-66°). Benzene is usually sulfonated by means of 100% or slightly fuming sulfuric acid (2 moles sulfuric acid to one of benzene) ; a temperature of 80-100° must be used at the end for completing the reaction; the sulfonator therefore carries a reflux condenser. The sulfonation of benzene is practised on an enormous scale, especially for phenol manufacture; and continuous processes, both in the liquid phase and the vapor phase, have also been developed.[4] In the Guyot or Tyrer process,[26] which is a batch process, benzene vapor is introduced into 90-92% sulfuric acid in a closed vessel, the temperature of the acid being first kept at 95-110°, then at 180°, and finally at 140-165°. Unsulfonated benzene and the water formed in the reaction distil and are condensed, and benzene is returned in vapor form to the sulfonator. By this method 97% of the sulfuric acid can be consumed.

Benzene-*m*-disulfonic acid (very deliquescent crystals), together with a small amount of the *p*-compound, is obtained by treating benzene or its monosulfonic acid with excess oleum. In presence of mercury the proportion of *m*- to *p*- is two to one.[27] The formation of the *p*-compound is kept to a minimum by sulfonating with oleum at a low temperature or with sulfuric acid at 240-250°, so as to shorten the reaction time. A mixture of sulfuric acid and sodium sulfate can be used. The technical method[6] is to monosulfonate benzene with monohydrate (100% H_2SO_4) at 40-100°, add 65% oleum and carry out the disulfonation at 80-85°. It is unnecessary to separate the *p*-acid since both the isomers give resorcinol by alkali fusion. A method of separation is to convert the disulfonic acids into the potassium salts and concentrate the solution to sp. gr. 1.275, when the *m*-salt separates.

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[25] See Chapter XXIX.

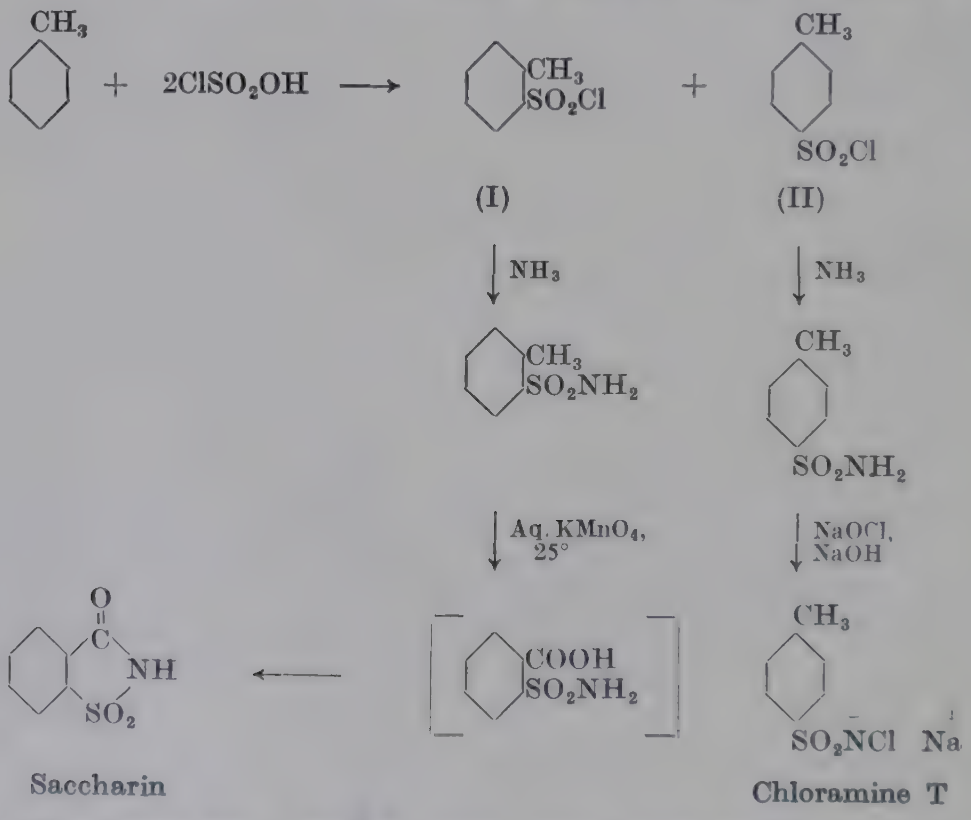
[4] See p. 50.

[26] Tyrer, USP 1,210,725; Maguire and Gould, USP 2,379,585.

[27] Behrend and Mertelsmann, *Ann.* **378**, 352 (1911).

Toluenesulfonic acids. Toluene sulfonates more readily than benzene, forming a mixture of the *o*- and *p*-acids. At low temperatures the *o*- is the major product, and at high temperatures the *p*- (m.p. 104-105°). Disulfonation gives toluene-2,4-disulfonic acid, used for oxidation to benzaldehyde-2,4-disulfonic acid.

Toluene-*o*- and *p*-sulfonyl chlorides (I and II) are obtained by the treatment of toluene with two or more moles of chlorosulfonic acid at about 20°. They are separated by freezing the mixture and removing the solid *p*-compound in a centrifuge. *p*-Toluenesulfonyl chloride (m.p. 71°) is useful for acylating amino and hydroxyl groups in certain intermediates and dyes as a method for improving fastness properties. *p*-Toluenesulfonamide is used for making the antiseptic Chloramine T. *o*-Toluenesulfonyl chloride (m.p. 67·5°) is used for making the well-known sweetening agent, saccharin. Methyl *p*-toluenesulfonate (m.p. 28°) is a useful methylating agent, and is prepared by adding aqueous caustic soda to a solution



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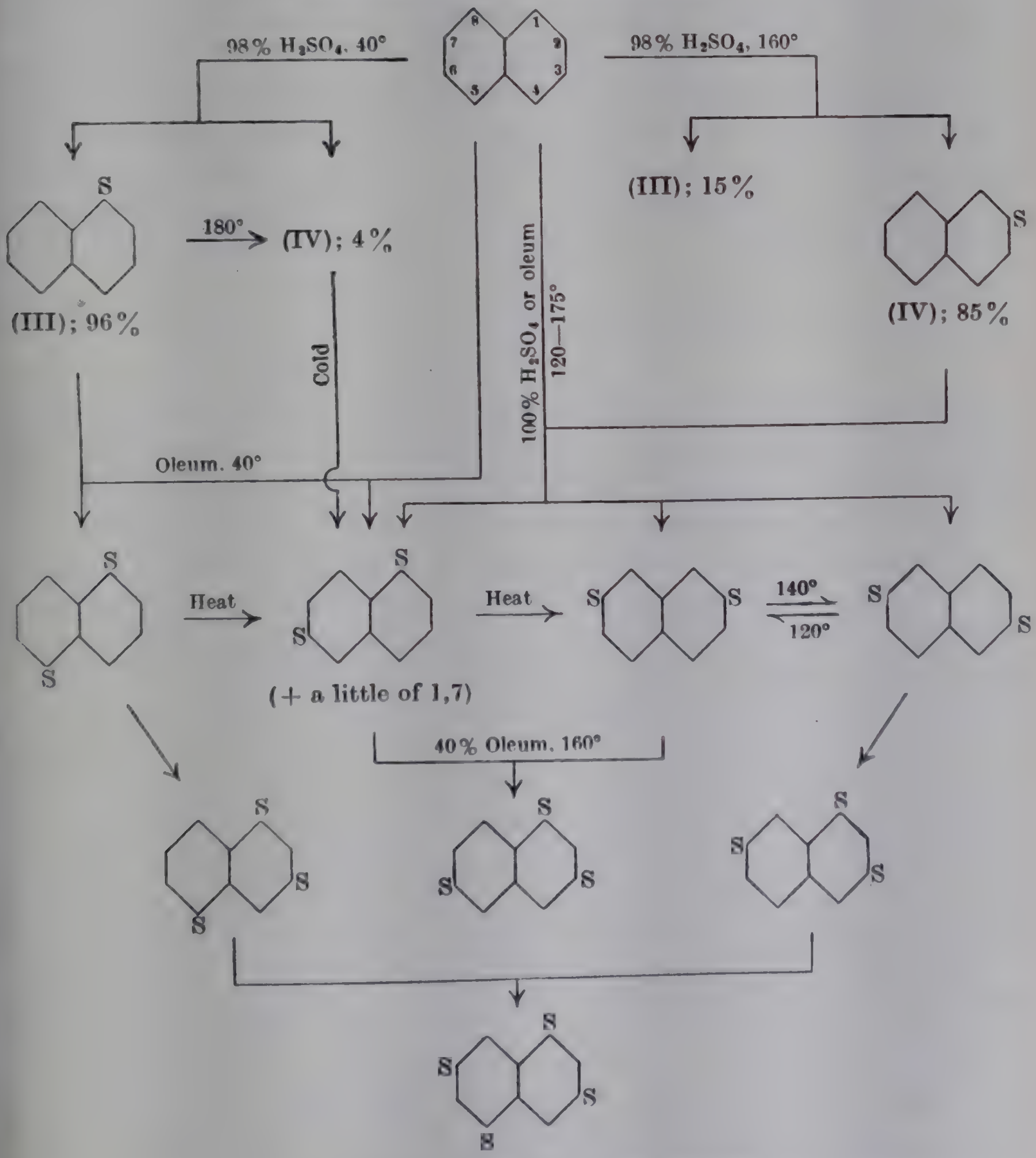
[6] See p. 50.

of *p*-toluenesulfonyl chloride in methanol at about 25°, and purifying the ester by vacuum distillation. *n*-Butyl and other esters, prepared similarly,[28] are useful as *O*-alkylating agents. Esters of *p*-toluenesulfonic acid are useful in the synthesis of *n*-alkylbenzenes; thus *n*-amylbenzene can be prepared by the action of *n*-butyl-*p*-toluenesulfonate on benzylmagnesium chloride.[29]

CHART 1

SULFONATION OF NAPHTHALENE*


98% H_2SO_4, 40°
1
2
3
4
5
6
7
8
98% H_2SO_4, 160°
S
180°
(IV); 4%
(III); 96%
Cold
100% H_2SO_4 or oleum
120—175°
(III); 15%
S
(IV); 85%
Oleum, 40°
S
S
Heat
S
S
(+ a little of 1,7)
Heat
S
S
140°
120°
S
S
40% Oleum, 160°
S
S
S
S
S
S
S
S
S
S
S
S
S

*S=SO_3H in the Charts in this chapter.

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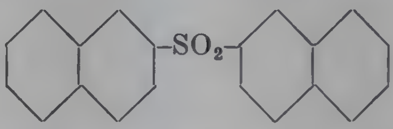
[28] Roos, Gilman, and Beaber, *OSCV* I, p. 145.

[29] Gilman and Heck, *JACS* **50**, 2223 (1928); Gilman and Robinson, *OSCV* II, p. 47.

Naphthalenesulfonic acids. Sulfonation of naphthalene invariably gives a mixture of α- and β-acids (III and IV), lower temperatures favoring α- and higher temperatures β-orientation (Chart 1).[30] When the α-sulfonic acid is heated with sulfuric acid, it slowly isomerizes to the β-sulfonic acid. Using the required quantity of 98% sulfuric acid for monosulfonation at 40°, 96% of the α- and 4% of the β-acid are formed. When the sulfonation mixture is diluted, limed and filtered, the filtrate contains the substantially pure calcium salt of the α-acid, which is more soluble than the calcium salt of the β-acid; and no further purification is usually necessary.[31] The β-acid may be removed as the sparingly soluble ferrous salt.[32] Sulfonating naphthalene with an equal weight of 96% sulfuric acid at 165°, the major product (85%) is the β-compound, but at such high temperatures a little 2,2′-dinaphthylsulfone (V) is also formed. Sodium sulfate solution is added, unsulfonated naphthalene is recovered by steam distillation, and the β-salt is salted out. This is pure enough for conversion into β-naphthol, but if it is not obtained completely free from the α-isomer in this manner, a method of removal of the α-acid from the sulfonation mixture is to blow dry steam into the charge at 160-165° when the α-acid alone is desulfonated to naphthalene, which comes over.[33] The β-acid crystallizes on cooling.



(V)

Naphthalene-α- and -β-sulfonic acids in admixture can be determined by bromination under specific conditions in which the β-acid is brominated to give a soluble product, while the sulfonic group in the α-compound is displaced by bromine so that the product is insoluble.[34] The mutual solubility effects of the lead salts of the two acids have also been used.[35]

Four disulfonic acids (1,5; 1,6; 2,6; 2,7) are formed by sulfonating naphthalene with monohydrate or with oleum, and the proportions vary with the temperature. The second sulfonic group enters the unsubstituted ring, but not in the *peri*-position; thus further sulfonation of the α-monosulfonic acid gives the 1,5-, 1,6- and 1,7-acids, and the β-acid gives the 2,5(1,6)-, 2,6-, 2,7- and 2,8(1,7)-acids. Naphthalene-1,2-, -1,4- and -1,8-disulfonic acids are not products of the sulfonation of naphthalene, but they can be prepared from the corresponding naphthylaminesulfonic acid through the diazonium salt and the sulfinic acid.[36] Naphthalene-1,3-disulfonic acid occurs[37] in the products of the sulfonation of naphthalene at 130°, and it has been prepared from β-naphthylamine-6,8- and 5,7-disulfonic acids by treatment of the corresponding hydrazine with boiling copper sulfate solution.[38]

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[30] Witt, *Ber.* **48**, 743 (1915); Fierz-David *et al.*, *Helv. Chim. Acta* **5**, 1146 (1923) and earlier papers; *J. Soc. Chem. Ind.* **42**, 421T; 425T (1923).

[31] For the preparation of pure naphthalene-α-sulfonic acid, see Fierz-David and Weissenbach, *Helv. Chim. Acta* **3**, 314 (1920).

[32] Geigy, BP 414,573.

[33] National Aniline Co., USP 1,922,813.

[34] Lantz, *Bull. soc. chim. France* (5) **2**, 1913 (1935).

[35] Euwes, *Rec. trav. chim.* **28**, 304 (1909); Witt, *Ber.* **48**, 754 (1915).

Below 40°, the main products are the 1,5-acid (77%) and the 1,6-acid (23%), together with a trace of the 1,7-acid. The 1,5-acid is separated as the barium salt, which is sparingly soluble in boiling water, whereas the 1,6-acid and 1,7-acid form soluble barium salts. The 1,5-acid is technically the most valuable of the naphthalenedisulfonic acids. It may be prepared by sulfonating naphthalene below 40° with 4-5 times its weight of 30-23% oleum. On dilution with about 4 parts of water, the 1,5-acid crystallizes and can be used without further purification.[39] Naphthalene-1,5-disulfonyl chloride is obtained in quantitative yield by treatment of naphthalene with 4 moles of chlorosulfonic acid.[40] One of the uses of naphthalene-1,5-disulfonic acid is the preparation of stabilized diazonium salts.[41] The 1,6-acid, recoverable from the filtrate after separation of the 1,5-acid, is also useful for this purpose.

As the temperature of sulfonation is raised, the 1,5-acid is transformed into the 1,6-acid. In 20% oleum below 100°, we get 75-80% of the 1,6-acid and 25-20% of the 1,7-acid. At 120-130°, the 1,6-acid and the 2,7-acid with a trace of the 1,5-acid are the products. At 140° there is no 1,5-acid at all, the 2,6- and 2,7-acids being the main products, together with a little of the 1,6-acid. The 2,6-acid can be separated as the barium or calcium salt, sparingly soluble in salt solution. At 165° the 2,7-acid is the major product (65%), accompanied by the 2,6-acid (25%) and the 1,6-acid (10%). The 2,6- and 2,7-acids are interconvertible by heating with sulfuric acid;[42] the 2,6- slowly goes over to the 2,7- on heating at 120°, and the reverse change takes place above 140°; at 170° an equilibrium mixture of equal proportions of the two acids is obtained. When the 2,7-acid is heated with 95% sulfuric acid at 160°, a maximum of 42% conversion into the 2,6-acid takes place in 19 hours.[42] The 2,7-acid, which is much more important technically as an intermediate for Naphthalene Green V, can be obtained in 42% yield (together with the 2,6- in about 22% yield) by heating naphthalene with thrice its weight of monohydrate at 170-175° for 5 hours, and then at 120° for 12 hours;[9] and in 50% yield by sulfonating naphthalene with 8 parts of 98% sulfuric acid at 160° for 5 hours.[43] Separation of the 2,6- and 2,7-acids can be effected by dilution and salting out, when the 2,6-salt separates first.[9] The 2,7-acid can be obtained in a yield of 75-85% by vapor-phase sulfonation of naphthalene at 220-230°, and under conditions in which the brief period of contact largely prevents the transformation into the 2,6-acid.[44]

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[36] Gattermann, *Ber.* **32,** 1156 (1899).

[37] Chuksanova, *Chem. Abstracts* **34,** 5834 (1940).

[38] Armstrong and Wynne, *Proc. Chem. Soc.* **6,** 13, 129 (1890).

[39] For the preparation of the pure acid, see Fierz-David and Hasler, *Helv. Chim. Acta* **6,** 1135 (1923).

[40] IG, DRP 466,441.

[41] See Chapter IV.

[42] Heid, *JACS* **49,** 844 (1927).

Further sulfonation leads to three trisulfonic acids, of which the most important is the 1,3,6-acid, an intermediate stage in the preparation of H-acid (1-amino-8-naphthol-3,6-disulfonic acid); this trisulfonic acid is produced by the action of 20-30% oleum at 180° or 40% oleum at 160° on the 1,6- or 2,7-disulfonic acids, or on naphthalene-2-sulfonic acid, but as mentioned later in connection with H-acid, it is usually prepared by the continued sulfonation of naphthalene without isolation of the intermediate sulfonic acids. The 1,3,5- and 1,3,7-acids are made from the 1,5- and 2,6-disulfonic acids respectively. These sulfonic acids are used as intermediates for naphtholsulfonic, naphthylaminesulfonic and aminonaphtholsulfonic acids. The ultimate product of the sulfonation of naphthalene is the 1,3,5,7-tetrasulfonic acid, which has no technical interest. In the tri- and tetrasulfonation of naphthalene, two sulfonic groups never enter adjacent (1,2- or 2,3-), 1,4- or 1,8 (peri)-positions.

The mechanism of the sulfonation of naphthalene has been widely studied.[45] It has been shown that the α-acid is the primary product, and the formation of the β-acid by sulfonation at high temperature is the result of hydrolysis of the α-sulfonic acid to naphthalene and sulfuric acid, followed by resulfonation. The course of sulfonation is therefore determined by (a) the relative velocities of formation of the α- and β-acids, and (b) the relative velocities of their desulfonation. The transformation of the 1,6-disulfonic acid into the 2,7- and the 2,6-acids takes place through the intermediate formation of the 1,7-acid; the latter results from the desulfonation of the 1,6-acid to the β-mono-acid and sulfonation of the latter to the 1,7-disulfonic acid. Hydrolysis again in the 1-position, followed by resulfonation, leads to the 2,7-acid. The equilibrium between the α- and β-acids is also influenced by the equilibria between sulfuric acid and its hydrates. The rate of further sulfonation of the α- and β-acids increases rapidly with increasing concentration of sulfuric acid, and with rise of temperature the β-acid sulfonates much faster than the α-acid. Mono- and disulfonations are exothermic, whereas tri- and tetrasulfonations are endothermic.

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[9] See p. 50.

[43] Simpson and Olsen, *Ind. Eng. Chem.* **29,** 1350 (1937).

[44] Ambler, Lynch, and Haller, *ibid.* **16,** 1264 (1924).

[45] Euwes, *Rec. trav. chim.* **28,** 298 (1909); Ambler, Lynch, and Scanlan, *Ind. Eng. Chem.* **19,** 417, 1010 (1927); Ioffe, *J. Gen. Chem.* (*U.S.S.R*)., **3,** 437, 565 (1933); Federov and Spruiskoo, *Org. Chem. Ind. U.S.S.R.* **2,** 100 (1936); Lantz, *Bull. soc. chim. France* (5) **12,** 253, 262 (1945); *ibid.* 95 (1947); Fierz-David and Richter, *Helv. Chim. Acta* **28,** 257 (1945); Hodgson, *J. Soc. Dyers Colourists* **63,** 46 (1947), *et sequa* ; Spryskov, *Zhur. Obshcheĭ Khim.* **18,** 98, 749, 941 (1948).

Monosulfonic acids of alkyl- and dialkylnaphthalene are largely used wetting agents. Nekal BX (IG) is the sodium salt of a dibutylnaphthalenesulfonic acid (probably 1,4-bis-*sec.*-butylnaphthalene-6-sulfonic acid)[45a], and products of a similar type are marketed by other manufacturers: e.g., Invadine B (Ciba) and Perminal BX and WA (ICI). The general method of preparation is to treat a mixture of naphthalene and the desired quantity of the appropriate alcohol with oleum. Thus Nekal BX is made[46] by adding 96% sulfuric acid (1.81 parts), followed by 24% oleum (2.4), to an agitated mixture of anhydrous *n*-butanol (1) and naphthalene (0.865) at 25°. After addition of the acid, the temperature is raised to 50°, and agitation continued for about 6 hours. On allowing the product to settle, two layers separate: one of Nekal BX acid and the other of sulfuric acid. The Nekal acid is separated, diluted, neutralized with caustic soda and bleached by the addition of sodium hypochlorite (12.5% active chlorine content; 0.35 part). Sodium sulfate is added, and the product taken down to dryness on a drum drier. Nekal A is the analog from isopropyl alcohol, and Nekal AEM, used as an emulsifying agent, is a mixture of Nekal A and glue. Condensation products of naphthalenesulfonic acids and alkylnaphthalenesulfonic acids with formaldehyde are valuable dispersing agents (e.g., Tamol NNO, IG) commonly employed for the dispersion of vat dyes.[12]

Anthraquinonesulfonic acids. The sulfonation of anthraquinone is of great importance technically, since many of the other anthraquinone intermediates are made from the anthraquinonesulfonic acids. The sulfonic groups in anthraquinonesulfonic acids can be replaced directly by hydroxyl, chlorine, and amino groups (*vide infra*), and even by methoxyl groups although in poor yield.[47] 1-Amino-4-*p*-toluenesulfonamidoanthraquinone-2-sulfonic acid can be converted quantitatively into the corresponding 2-alkoxy compounds, which yield pure 1,4-diamino-2-alkoxyanthraquinones by hydrolysis with sulfuric acid.[48] Unlike anthracene which sulfonates readily with cold concentrated sulfuric acid, anthraquinone is unaffected by 96% acid at 100° and sulfonation begins only at about 200°. Anthraquinone with sulfur trioxide at 150-170° gives the 2-monosulfonic acid in good yield; little action occurs at 130°, and at 200° much hydroxyanthraquinonesulfonic acid is formed.[49] By heating with 20-25% fuming sulfuric acid at 140° for 8 hours the 2-monosulfonic acid is formed, but under these conditions, if sufficient acid is employed for complete sulfonation, exclusive monosulfonation is not possible. To avoid disulfonation, therefore, it is necessary to sulfonate under conditions in which 50% or more of the anthraquinone remains unattacked. Typical conditions used in practice[11] are to heat anthraquinone with an equal weight of 20% oleum at 100-110° for 3 hours, raise to 145° in 6 hours, and dilute with water (twice the weight of the anthraquinone). The mixture is filtered at 70° to recover anthraquinone. The unreacted anthraquinone sometimes tends to separate in a slimy condition, difficult to filter; but crystalline, readily filterable anthraquinone may be obtained by adding sulfuric acid first to dissolve the anthraquinone and precipitating slowly with water.[50] The sodium salt (" silver salt "), isolated by salting out directly with brine, crystallizes in silvery leaflets; by careful control of the salting-out process, silver salt of excellent purity can be obtained in a yield of about 90%, the more soluble sodium salts of the 2,6- and 2,7-disulfonic acids remaining in solution. It is an important intermediate for the preparation of Alizarin and of β-aminoanthraquinone.

[45a] *FIAT* **528.**

[46] *BIOS* **421.**

[12] See p. 50.

[47] DRP 156,762; Barnett and Goodway, *Ber.* **63**, 3048 (1930).

[48] IG, BP 359,397.

Anthraquinone-α-sulfonic acids were unknown until 1903, when Iljinsky[51] discovered that sulfonation in presence of mercury salts gave the α-mono- and the 1,5- and 1,8-disulfonic acids. The first effect of the intervention of mercury appears to be the formation of an α-mercuri derivative, the mercuri group being subsequently replaced by the sulfonic group.[52] Abnormal orientations in other sulfonations (e.g., nitrobenzene and phthalic anhydride) owing to the influence of mercury have also been noticed.[52] The α-monosulfonic acid (m.p. 218°) is prepared by heating anthraquinone with 1.5 parts of 18% oleum and a little mercuric oxide; formation of the β-acid can be suppressed by vigorous agitation to ensure complete dispersion of mercuric sulfate, which is very sparingly soluble in sulfuric acid. The temperature is raised to 120° in 2 hours, 60% oleum is added, and the heating continued at about 150° for a further 2 hours. Disulfonation can be largely avoided by suitable adjustment of conditions. The melt is

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[49] Schwenk, *Angew. Chem.* **44**, 912 (1931).

[11] See p. 50.

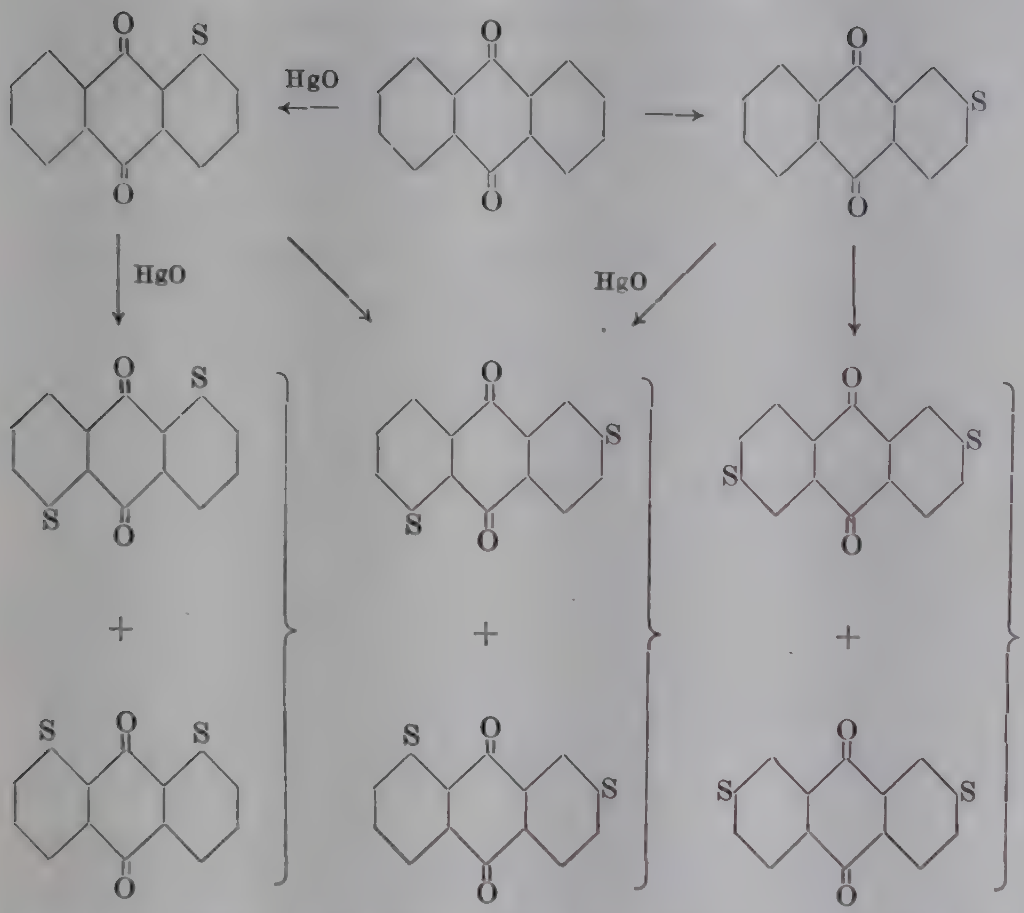
[50] Barnard, USP 1,474,507.

[51] *Ber.* **36**, 4194 (1903); Schmidt, *ibid.* **37**, 66 (1904).

[52] Lauer, *J. prakt. Chem.* (2) **130**, 185 (1931); *ibid.* **135**, 164 (1932). See also Kozlov, *J. Gen. Chem. U.S.S.R.* **18**, 2094 (1948).

CHART 2

SULFONATION OF ANTHRAQUINONE



poured into ice water, the precipitated anthraquinone filtered off, and the filtrate treated with potassium chloride, when the potassium salt crystallizes.[52, 53, 54]

Anthraquinone-2,6- and -2,7-disulfonic acids are obtained by the further sulfonation of the 2-monosulfonic acid. The 2,6-acid is the main product when anthraquinone is heated at 150° for 4-5 hours with 48% oleum (2-4 parts) and anhydrous sodium sulfate (0.25 part). Further sulfonation of anthraquinone-2-sulfonic acid in presence of mercuric oxide gives the 2,5(1,6)- and 2,8(1,7)-disulfonic acids. Further sulfonation of the 1-monosulfonic acid in presence of mercury yields the 1,5- and 1,8-disulfonic acids (Chart 2). These two disulfonic acids can be prepared[11] directly from anthraquinone by adding anthraquinone (16 parts) and 65% oleum (18 parts) to a solution of mercury (0.16 part) in 96% sulfuric acid or 5% oleum (13.7 parts) and 65% oleum (5.6 parts), and heating at 125° for 4 hours. When the melt is run into 84% sulfuric acid (29 parts) and cooled to 45°, the 1,5-acid precipitates; it is filtered off, washed with 78% sulfuric

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[52] See p. 60.

[53] Fierz-David, *Helv. Chim. Acta* **10**, 197 (1927).

[54] Scott and Allen, *OSCV* II, p. 539.

[11] See p. 50.

acid, dissolved in water, clarified and precipitated as the sodium salt by means of common salt. By adding potassium chloride solution to the mother liquor, the potassium salt of the 1,8-acid is precipitated. The yields of 1,5- and 1,8-acids, as the disodium and dipotassium salts, are about 39 and 26% respectively. The 1,5- and 1,8-disulfonic acids are said to be formed under milder conditions if the sulfonation mixture contains ammonium sulfate or a sulfate of an alkali or alkaline earth metal or magnesium.[55] A characteristic of all the anthraquinonedisulfonic acids is the complete deactivation of the anthraquinone system. The disulfonic acids cannot be further sulfonated and they cannot be nitrated; treatment with oleum at high temperatures results in nuclear hydroxylation (the Bohn-Schmidt reaction).[56]

The chloroanthraquinones sulfonate first in the unsubstituted nucleus. Thus α-chloroanthraquinone gives a mixture of about equal parts of the 6- and 7-sulfonic acids, readily separable on account of the much greater solubility of the sodium salt of the latter. Disulfonation yields the 2,6-, 4,6- and 2,7-acids. In presence of mercury the products are the 5-monosulfonic acid and the 2,5- and 4,5-disulfonic acids. Sulfonation of β-chloroanthraquinone gives the 6- and 7-monosulfonic acids and the 3,6- and 3,7-disulfonic acids.

CHARACTERIZATION OF THE SULFONIC ACIDS

Aromatic sulfonic acids form salts with arylamines, and these salts, which crystallize well and have melting or decomposition points, can be used for characterizing both sulfonic acids and amines.[57] The arylamine salts are prepared by mixing hot concentrated solutions of the sodium arylsulfonate and the arylamine (e.g., *p*-chloroaniline, α- and β-naphthylamine, benzidine) hydrochloride, when the salt usually crystallizes out on cooling. The salts can be recrystallized from water or very dilute hydrochloric acid, and they can be estimated by titration with caustic soda solution, since they are thus decomposed quantitatively to the sodium arylsulfonate and the arylamine. The *S*-benzylthiuronium salts of sulfonic acids are well-defined, crystalline compounds with characteristic sharp melting points.[58]

$$\begin{tikzcd}
\mathrm{Ar{-}SO_3Na + Ar'NH_2,HCl} \arrow[r] & \mathrm{ArSO_3^-H_3\overset{+}{N}Ar' + NaCl} \arrow[d, "\mathrm{NaOH}"] \\
 & \mathrm{ArSO_3Na + Ar'NH_2 + H_2O}
\end{tikzcd}$$

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[55] National Aniline Co., USP 1,963,383.

[56] See Chapter XXVIII.

[57] Forster and Keyworth, *J. Soc. Chem. Ind.* **43**, 165T (1924), *et sequa*.

[58] Chambers and Watt, *J. Org. Chem.* **6**, 376 (1941). For the characterization of sulfonic and sulfinic acids as thallous salts, see Gilman and Abbott, Jr., *JACS* **71**, 659 (1949).

Sulfonic acids react with phosphorus pentachloride to form sulfonyl chlorides, which melt at characteristic temperatures and which condense with primary and secondary amines to form sulfonamides (Hinsberg, 1890). By more drastic treatment with phosphorus pentachloride, sulfonic groups are replaced by chlorine ($ArSO_3H + PCl_5 \longrightarrow ArCl + HCl + SO_2 + POCl_3$). In the anthraquinone series, sulfonic acids and the sodium sulfonates are best characterized as the corresponding chloro compounds into which they are smoothly converted by treatment in aqueous solution with sodium chlorate and hydrochloric acid ($AQSO_3Na + 2[Cl] + H_2O \rightarrow AQCl + NaHSO_4 + HCl$). The monochloro and dichloroanthraquinones crystallize readily and have sharp melting points. When the disodium salts of anthraquinone-2,6- and 2,7- disulfonic acids are treated with nascent chlorine, only one sulfonic group is replaced, and the insoluble sodium 2-chloroanthraquinone-6- and -7-sulfonates separate; these may then be characterized as the arylamine salts (e.g., with *p*-chloroaniline) or by conversion into the corresponding sulfonyl chlorides, which however have melting points very near each other (203 and 201°). A distinction between α- and β-sulfonic acids of anthraquinone is their behavior in boiling alkali solution in the presence of an alkylmercaptan; the α-sulfonates are converted into thioethers ($AQSO_3Na + R\text{–}SNa \longrightarrow AQSR + Na_2SO_3$), which separate quantitatively after a few minutes' heating under suitable conditions; the β-sulfonates do not react. Sodium anthraquinone-α-sulfonate present in "silver salt" can be quantitatively estimated in this manner. Anthraquinone-1,8-disulfonic acid readily forms the dithioether, but in the case of the 1,5-acid, the sparingly soluble 5-thioether of sodium anthraquinone-1-sulfonate separates. Like other thioethers, the anthraquinonyl alkyl sulfides are readily oxidized to the sulfones on treatment with nitric acid ($AQSR \longrightarrow AQSO_2R$). Another useful reaction of the sulfonic acids, to which several references have also been made elsewhere, is their hydrolysis ($ArSO_3H + H_2O \longrightarrow ArH + H_2SO_4$) by a variety of reagents, e.g., boiling dilute sulfuric acid or sodium amalgam. The specific behavior of the α- and β-sulfonic acids of naphthalene, the naphthols, and the naphthylamines is mentioned in the relevant sections of this chapter. In the anthraquinone series, α-sulfonic groups are more mobile than the β-; thus, by heating with concentrated sulfuric acid at 200° for a few hours desulfonation takes place in the α- but not in the β-position, unless there are hydroxyl or amino groups adjacent to the β-sulfonic groups. Both α- and β-sulfonic groups are removed by heating with 80% sulfuric acid in presence of mercury or boric acid, but the α more readily.[59]

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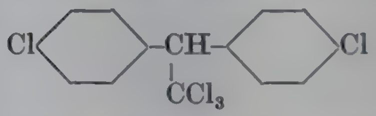
[59] Fierz-David, *Helv. Chim. Acta* **10**, 225 (1927).

HALOGENATION

Benzene, toluene, and the xylenes react with chlorine with or without the addition of a carrier. It is obvious that in the alkylbenzenes both nuclear and side-chain chlorination can occur according to the conditions, which therefore must be specified and controlled. Phenols are chlorinated much more readily than the hydrocarbons, e.g., by sodium hypochlorite solution followed by acidification of the mixture; some amines can also be chlorinated in this manner, but the *N*-acyl derivatives are usually employed for halogenation. The Sandmeyer reaction for the replacement of an amino group by chlorine *via* the diazonium salt can be used in special cases, such as the conversion of H-acid into 1-chloro-8-naphthol-3,6-disulfonic acid. In the anthraquinone series chloro compounds are prepared by the action of chlorine on the sodium sulfonates.

Chlorobenzene (b.p. 132°) is an important primary intermediate from which the chloronitrobenzenes, aniline, and phenol are prepared. Further, chlorobenzene is a useful solvent, and it is manufactured on a large scale for conversion into DDT, which is at present the most widely used domestic agricultural, and horticultural insecticide. Benzene is chlorinated at the boiling point in presence of about 1% of its weight of iron powder (or ferric chloride); iodine and the chlorides of aluminium, antimony, and molybdenum are other catalysts. Batch and continuous processes are both in vogue. A problem in large-scale chlorinations is the absorption and disposal of the hydrochloric acid evolved ($ArH + Cl_2 \longrightarrow ArCl + HCl$). The absorbers are best made of tantalum. The recovered hydrochloric acid is utilized in other parts of the plant, but frequently the quantities thus available are far in excess of requirements. In the chlorination of benzene, exclusive monochlorination is not possible, and the chlorination product contains benzene, *p*-dichlorobenzene (m.p. 53°; b.p. 174°) and *o*-dichlorobenzene (b.p. 180.3°) in proportions depending on the chlorinating conditions. After washing free from dissolved hydrogen chloride, pure chlorobenzene is isolated by fractional distillation, *o*- and *p*-dichlorobenzenes being simultaneously separated. *p*-Dichlorobenzene, which is a useful insecticide and a more valuable dye intermediate than the *o*-compound, can be separated from its mixtures with the *o*-compound by treatment below 15° with chlorosulfonic acid, when only the *o*-compound is attacked with formation of a sulfonyl chloride,[60] or the treatment can be limited to the eutectic mixture of the two dichlorobenzenes at 20-25°.[61] Since the *p*-compound



DDT

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[60] Bennett and ICI, BP 440,205

[61] Monsanto Chemical Co., USP 1,993,722.

is a solid and the *o*- an oil, the usual process for separation is a "sweating" treatment, followed by further purification by distillation. "Sweating" is a method of separation in which a mixture, after being set to a solid by cooling, is slowly warmed to a temperature at which one or more of the constituents liquefy and can be drained off.

***m*-Dichlorobenzene** (b.p. 172°) can be prepared by an unusual reaction;[6] it is obtained in about 80% yield when dry chlorine is led into molten dinitrobenzene at 220° in a glass tube. Condensation of the vapors gives a mixture of *m*-dichlorobenzene (68%), *m*-chloronitrobenzene (25%), trichlorobenzene (2%) and unconverted dinitrobenzene (5%). The product is washed with sodium carbonate solution and fractionated in vacuum, *m*-chloronitrobenzene and dinitrobenzene being recycled. Another route to *m*-dichlorobenzene is the further chlorination of chlorobenzene at 500-600° in presence of pumice, which gives a product containing 50-60% of *m*-dichlorobenzene.[62]

1,2,3-Trichlorobenzene (m.p. 53-54°; b.p. 218-219°) and **1,2,4-trichlorobenzene** (m.p. 17°; b.p. 213°) are obtained by further chlorination of *o*-dichlorobenzene in presence of sublimed ferric chloride at 30° until the specific gravity at 15° reaches 1.40. The isomers are then separated by fractional distillation and sweating.[6] 1,2,4-Trichlorobenzene can also be prepared by chlorinating benzene in presence of iron filings, first at 20-30° and then at 55-65°, until the specific gravity at 50° reaches 1.335; alternatively, *p*-dichlorobenzene can be used as starting material.[10]

The action of chlorine on benzene in presence of sunlight and in the absence of catalysts and oxygen leads to benzene-hexachloride, a mixture of five isomers of which 65-70% is the α-isomer and 10-12% the γ-isomer; the latter is the main insecticidal principle of Gammexane (ICI), which is a notable addition to the available range of insecticides.[63]

Fluorobenzene, made by the action of sodium nitrite and hydrogen fluoride on aniline hydrochloride at 10-40°, is used for making the insecticide Gix (IG), the fluorine analog of DDT.

Chlorination of toluene[64] in presence of sublimed ferric chloride, or other carriers mentioned earlier, maintaining the temperature below 30°, leads to nuclear substitution, *o*- and *p*-chlorotoluenes (I and II) being formed in approximately equal amounts. Chlorination is regarded as being complete when the sp. gr. is 1·06 at 20°. The two isomers, differing in b.p. by only 3°, can be separated by controlled sulfonation, when the

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[6] See p. 50.

[62] Wibaut *et al.*, *Rec. trav. chim.* **56**, 65 (1937).

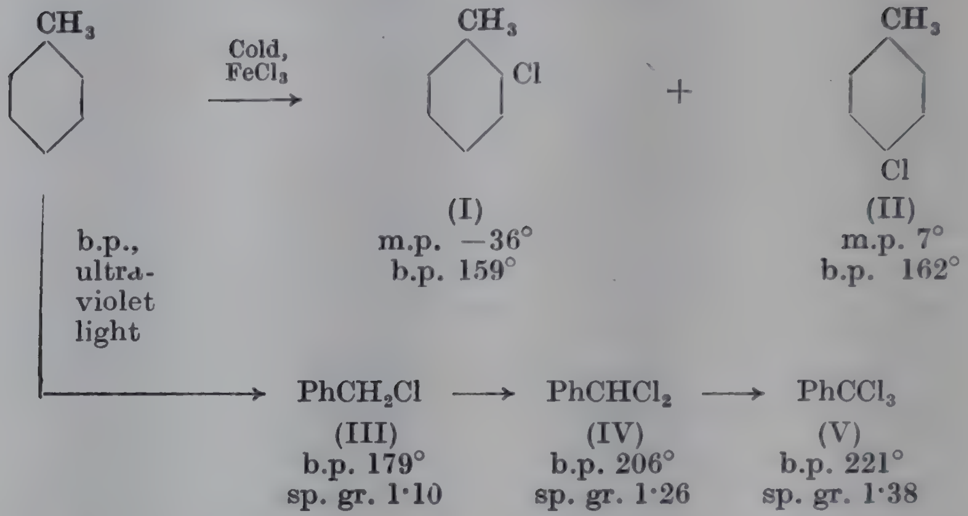
[6, 10] See p. 50.

[63] Ramsey and Patterson, *J. Assoc. Offic. Agr. Chemists* **29**, 337 (1946); Kauer *et al.*, *Ind. Eng. Chem.* **39**, 1335 (1947).

[64] *BIOS* **1145.**

CHART 3

CHLORINATION OF TOLUENE



o-compound alone is sulfonated; the sulfonic acid is isolated and desulfonated by means of superheated steam. On the large scale, however, separation of *o*- and *p*-chlorotoluene, after removal of benzyl chloride by treatment with 35% aqueous caustic soda (5% of the weight of the mixture) at 120° for 24 hours, is effected[64] by careful fractionation into two main fractions containing respectively 90% of the *ortho* and 90% of the *para* isomer; on redistillation the former gives essentially pure *o*-chlorotoluene, while pure *p*-chlorotoluene is obtained from the latter by sweating at −5°. *o*-Chlorotoluene is used for making *o*-chlorobenzaldehyde, an intermediate for some triphenylmethane colors. *m*-Chlorotoluene (b.p. 162°) is manufactured from *m*-toluidine by the Sandmeyer reaction. A laboratory method for the preparation of *m*-chlorotoluene is to monochlorinate *p*-toluidine which gives 3-chloro-*p*-toluidine, and remove the amino group by diazotization and reduction with alcohol.[65] Further chlorination of *p*-chlorotoluene gives a mixture of 2,4- and 3,4-dichlorotoluenes, which can be separated by fractional distillation.[6]

Substitution of toluene in the side chain is effected by carrying out the chlorination at the boiling point during exposure to light, and with the addition of about 2% of phosphorus trichloride as carrier. Since contact with iron must be avoided, the reaction kettle is glass lined or enameled, or it may be made of nickel. The vessel is provided with a reflux condenser of similar construction or of glass, and a glass bell or tube containing one or more 300-500 watt electric bulbs, emitting light rich in ultraviolet rays, is fitted into the cover. The progress of the chlorination is followed from the specific gravity of the product, the chlorination being stopped at the stage when the product is mainly benzyl chloride (III) or a mixture of benzal chloride (IV) and benzotrichloride (V); in either case all three compounds are present, as well as a little toluene and nuclear chloro compounds. Complete chlorination to (V) is not attempted, since the chlorination is very slow towards the end and nuclear chlorination is likely to take place. The three chlorides are produced in the pure state by fractional distillation. Benzyl chloride is used as a benzylating agent for amines, while (IV) and (V) lead to benzaldehyde and benzoic acid; (V) is also useful for making benzoyl chloride. Benzyl chloride is used in large quantities for making quaternary ammonium salts from tertiary amines such as dimethyldodecylamine ; these salts, e.g., Roccal ($C_{12}H_{25}\overset{+}{N}Me_2CH_2Ph\ Cl^-$), are powerful disinfectants. By side-chain chlorination of *o*- and *p*-chlorotoluene and 2,4-dichlorotoluene, the corresponding nuclear chlorinated benzal chlorides and benzotrichlorides are prepared, and used for conversion into the corresponding benzaldehydes, benzoic acids, and benzoyl chlorides.[64]

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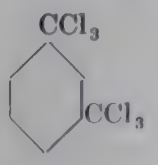
[64] See p. 65.

[65] The preparation of *m*-bromotoluene in this manner is described by Bigelow, Johnson, and Sandborn, *OSCV* I, p. 133.

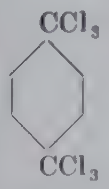
[6] See p. 50.

An interesting method of side-chain chlorination of toluene in the absence of light is the action of sulfuryl chloride[66] on boiling toluene in presence of about 0.005 mole of benzoyl peroxide.[67] Thus toluene gives a nearly theoretical yield of benzyl chloride in 15 minutes, and the chlorination can be continued to give benzylidene chloride, but not benzotrichloride; no nuclear chlorination occurs with toluene or with *m*-xylene.[67]

Xylenehexachlorides. Side-chain chlorination of *m*- and *p*-xylene produces the corresponding hexachlorides (VI and VII), which, like benzotrichloride, are useful for the preparation of the acid chlorides and the carboxylic acids (isophthalic and terephthalic acids).



(VI)



(VII)

Intermediates (e.g., VIII) containing the trifluoromethyl (CF_3) group have been used recently,[68,69,70] and the fluoro group is introduced by the action of 98% hydrofluoric acid under pressure on the corresponding chloro compound (e.g., IX). The mixture is heated in a steel autoclave at 100-110° when there is a sharp rise in pressure to about 25 atm., and the hydrogen chloride evolved is led off through a needle valve at such a rate that the reaction takes 8-10 hours. Hydrofluoric acid vapor is condensed and returned to the autoclave. Iron and steel vessels and pipes are suitable for handling hydrofluoric acid, but a nickel-plated still and column are used for trifluoromethylbenzoyl fluoride (XI), and in some cases pipes and connections are made of synthetic resins.[6]

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[64] See p. 65.

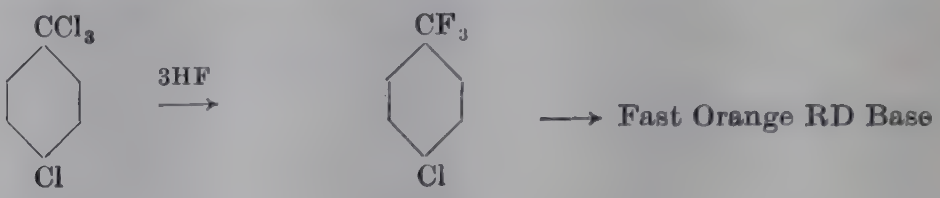
[66] For a review of the properties of sulfuryl chloride, including halogenation, see Brown, *Ind. Eng. Chem.* **36,** 785 (1944).

[67] Kharasch and Brown, *JACS* **61,** 2142 (1939).

[68] See Chapters XXII and XXXI.

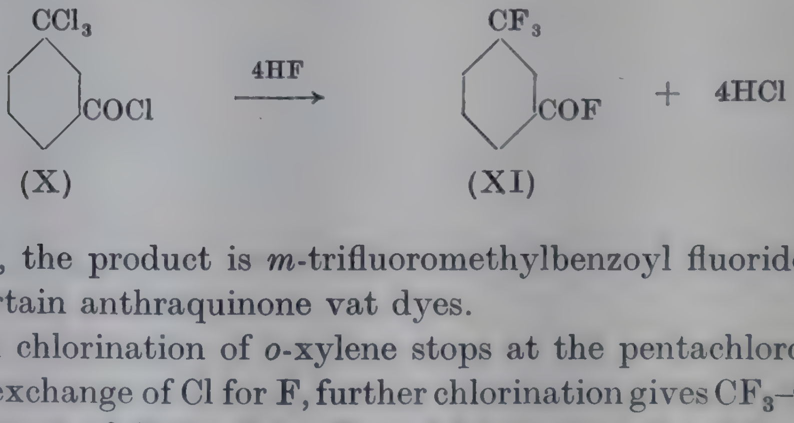
[69] Recent interest in fluorine compounds, arising primarily from the valuable properties of difluorodichloromethane (" Freon ") as a refrigerant, is shown by the series of papers in *Ind. Eng. Chem.* **39,** 290 (1947); Organic Compounds of Fluorine have been reviewed by Smith, *Annual Repts. Chem. Soc. London*, **44,** 86, 1947.

[70] Kuhlmann, BP 540,597; IG, BP 452,436; 459,881; 459,890; 479,774; 480,105.



(IX) (VIII)

The action of one mole of water on *m*-xylenehexachloride (VI) yields *m*-trichloromethylbenzoyl chloride (X), and when this is heated with anhydrous hydrofluoric acid at about 30 atm. pressure, first at 30° and finally at 80°, the product is *m*-trifluoromethylbenzoyl fluoride (XI), used in making certain anthraquinone vat dyes.



(X) (XI)

Side-chain chlorination of *o*-xylene stops at the pentachloro derivative, but after the exchange of Cl for F, further chlorination gives $CF_3–C_6H_4–CF_2Cl$. The displacement of Cl by F is effected by heating the chloro compound with a double fluoride of antimony in a high-boiling solvent.[71]

In the monochlorination of naphthalene the main product is α-chloronaphthalene, the β-chloro compound being formed to the extent of 8-10%. The isomers can be isolated by freezing out the α-compound and crystallizing the β- from the eutectic.[72] α-Alkyl and α-halogenonaphthalenes isomerize easily to the β-compounds by passage over a catalyst at a moderately high temperature.[73] α- and β-Chloronaphthalenes have no technical interest, but the polychloronaphthalenes have waxy properties for which they have found use in industry. Bromination of naphthalene in boiling carbon tetrachloride, followed by fractional distillation, gives α-bromonaphthalene (b.p. 281°) in 75% yield.[74]

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[6] See p. 50.

[71] IG, BP 465,885.

[72] Britton and Reed, USP 1,917,822.

[73] Mayer and Schiffner, *Ber.* 67, 67 (1934).

The halogenation of substances other than hydrocarbons and the preparation of halogenated compounds by methods other than direct halogenation are mentioned later. Examples are the preparation of dichloro- and tetrachlorophthalic anhydride, chlorophenols, chloroanilines, 2-chloro-3-aminoanthraquinone, 4-bromo-1-aminoanthraquinone-2-sulfonic acid, and 2,4-dibromo-1-aminoanthraquinone. The halogenation of anthraquinone is so difficult as to be impracticable, and the chloroanthraquinones are prepared through the sulfonic acids or by synthesis by the phthalic anhydride route, but the aminoanthraquinones can be directly halogenated. The chlorination and bromination of dyes (and iodination of a few phthalein dyes) are important methods for producing brighter shades with improved fastness, especially to light and chlorine.

NITRATION

By the action of concentrated nitric acid on aromatic compounds nuclear substitution by a nitro group takes place with the formation of water ($\text{Ar-H} + HNO_3 \longrightarrow \text{Ar-}NO_2 + H_2O$), and since dilute nitric acid is an oxidizing agent, nitration is usually carried out by means of a mixture of nitric and sulfuric acids (" mixed acid ").[75] The active nitrating agent is the nitronium ion ($HNO_3 + 2H_2SO_4 \longrightarrow NO_2^+ + H_3O^+ + 2HSO_4^-$), so that the function of sulfuric acid is not merely the removal of water.[76] The rate of nitration varies with the nature of the compound. Di- and trinitration proceed much less readily than mononitration, requiring stronger mixed acid and higher temperatures. A continuous process for nitrating benzene with 61% nitric acid, no sulfuric acid being employed, and removing the water formed as an azeotropic mixture with benzene, has been described; using distillation under reduced pressure, toluene can be similarly nitrated.[77] A 25% conversion of benzene into nitrobenzene is obtained by passing the mixed vapors of benzene and nitric acid over calcium phosphate at 175°.[78] A 45% yield of *p*-nitrotoluene can be obtained by nitration with ethyl nitrate ($\text{Et–O–}NO_2$) in presence of 98% sulfuric acid.[79] While the normal function of sulfuric acid in nitration is to remove the water formed, it sometimes takes part in the reaction, and in the naphthalene and anthracene series sulfonation preceding nitration has been observed. In the preparation of picric acid, phenol is first converted into the 2,4-disulfonic acid, which is then nitrated with mixed acid, and oxidation of the phenol is prevented in this manner. Glacial acetic acid and acetic anhydride can be used as solvents in laboratory nitrations, and examples of other special methods are the use of benzoyl nitrate, the Sandmeyer reaction in which a diazonium nitrate is treated with nitrous acid in presence of a copper salt, and the treatment of a hydrocarbon with nitric oxide in presence of aluminium chloride.[79a]

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[74] Clarke and Brethen, *OSCV* I, p. 121.

[75] For a review of aromatic nitration, see Gillespie and Millen, *Quart. Revs.* **2**, 277 (1948).

[76] Bennett, *JCS* 869 (**1946**); *Chemistry and Industry* 235 (1949); Westheimer and Kharasch, *JACS* **68**, 1871 (1946); see also Melander, *Nature* **163**, 599 (1949); Ingold *et al., ibid.*

[77] Othmer *et al., Ind. Eng. Chem.* **34**, 286 (1942); Kokatnur, USP 2,435,314.

[78] Rout and ICI, BP 586,732.

In a technical nitration the order in which the reagents are added, agitation of the reaction mixture, and efficient cooling are methods by which the process is regulated and controlled. Thus mixed acid may be added to the substance to be nitrated (benzene); the finely powdered substance is added to the mixed acid (naphthalene); nitric acid or mixed acid is added to a solution of the substance in sulfuric acid (acetanilide; phenolsulfonic acids); or potassium nitrate is added to a solution of the substance in sulfuric acid, if it is readily oxidizable (benzaldehyde).

Nitrobenzene.[6, 80] The purity of the benzene and toluene used for nitration has been specified earlier.[81] The approximate percentage composition of the mixed acid for nitrating benzene is nitric acid 30, sulfuric acid 60, and water 10, made up from acids of any convenient strength. For one part of benzene, 2.5-3 parts of mixed acid are used. Nitration is carried out in a closed cast iron kettle, provided with a propeller type of stirrer having a speed of at least 60 r.p.m., an inlet for the mixed acid, cast iron thermometer tube, a bottom discharge, a cooling jacket, and internal cooling coils of lead. Benzene is first run in, the agitator started, cooling water circulated, and the cooled mixed acid run in slowly so that the temperature is kept below 25-30°. Towards the end of the process, the temperature is raised to 70-80°. The progress of the nitration is followed by draining off a sample of the mixture, separating the layers of nitrobenzene and acid and determining the specific gravity of the nitrobenzene or the nitric acid content of the acid in a Lunge nitrometer. The quantity of nitric acid employed is such that the spent acid, when nitration is nearly complete, contains about 1% nitric acid ; and it is also common practice in order to avoid dinitration to leave a little unnitrated benzene, which is readily recoverable by fractional steam distillation of the nitration product. The agitator is then stopped, the mixture allowed to settle for a few hours, and the spent acid drawn off at the bottom. The spent acid is extracted with benzene to recover dissolved and emulsified nitrobenzene. The recovery of sulfuric acid by denitration of the spent acid and concentration is important in the economy of nitration processes. Crude nitrobenzene is washed free from acid and steam-distilled until all the benzene has come over. The residual nitrobenzene can be used directly for reduction or purified further by steam distillation followed by distillation in vacuum. The yield is about 98%. In view of the importance of nitrobenzene as a primary intermediate, solvent, and oxidizing agent, much attention has been paid to the design of nitration plant and to the details of manufacturing conditions,[82] but the simple type of cast iron batch nitrator is well established.

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[79] ICI, USP 2,416,974.

[79a] See also Hodgson, Heyworth and Ward, *J. Soc. Dyers Colourists* **66**, 229 (1950).

[6] See p. 50.

[80] *BIOS* 1144.

[81] Chapter II.

Nitrobenzene is a colorless hygroscopic liquid, b.p. 210°, m.p. 5·7°, d_4^{25} 1.197, volatile in steam, immiscible with water, and has a characteristic odor for which it is used as a cheap perfume (" oil of mirbane "), e.g., in soaps. As a solvent, especially in the preparation of acylamidoanthraquinones and the Ullmann reaction for the preparation of anthrimides, it is largely used; but precautions are necessary on account of its high toxicity resulting in cyanosis, both as vapor by inhalation and as liquid by skin absorption. In fact, all the nitro compounds of benzene and toluene are highly toxic. Absorption through the skin takes place rapidly, and contact with the liquid or solid substances, as well as exposure to the vapors, should be avoided. The factory acts usually require various precautions, such as the provision of special clothing for the workers.

Nitro compounds as a class can be estimated by reduction to the corresponding amines by means of an excess of titanous chloride in boiling acid solution in a current of carbon dioxide, the excess of the reducing agent being then determined by titration with ferric alum (potassium sulfocyanide indicator).[83] Nitrobenzene and other insoluble nitro compounds are sulfonated, prior to reduction and titration. By the use of sodium acetate or citrate buffer, reduction of nitro compounds (e.g., dinitrotoluene) by means of titanous chloride takes place rapidly at room temperature.[84]

***m*-Dinitrobenzene** (yellow needles, m.p. 91°, b.p. 302.8°). The dinitration of benzene can be effected in one operation,[85] but nitration in two stages is usually preferred.[86] The nitration of nitrobenzene is started at 40° with a stronger " mixed acid " than that used for mononitration;

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[82] *BIOS* **1246.**

[83] Knecht and Hibbert, New Reduction Methods in Volumetric Analysis, 2nd ed., Longmans, London, 1925.

[84] Butts *et al.*, *Anal. Chem.* **20,** 947 (1948).

[85] Hough *et al*, *Chem. & Met. Eng.* **23,** 668 (1920).

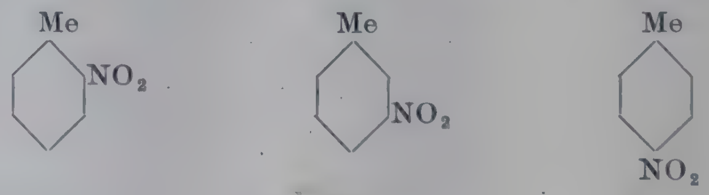
[86] Rhodes and Nelson, *Ind. Eng. Chem.* **30,** 648 (1938). For a study of the nitration of nitrobenzene, following the technique of thermal analysis, see Mason *et al.*, *JCS* 105 (**1933**); 1352, 1357 (**1934**).

the temperature is ultimately raised to 90° and then maintained until the odor of nitrobenzene disappears. The crude nitration product contains 85-90% of *m*-dinitrobenzene, the remainder being the *o*- and *p*-compounds, chiefly the former. A method of purification is to heat with a solution of sodium sulfite and bisulfite at about 70°; pure *m*-dinitrobenzene separates on cooling.[6, 87] Another method is to take advantage of the hydrolysis of the *o*- and *p*-compounds by 10% caustic soda solution at 100° to the nitrophenols, which then remain in solution. These isomers are also more soluble in alcohol and in benzene, and they may be removed by treatment of the crude nitration product with a limited amount of the hot solvent. *m*-Dinitrobenzene is used for making *m*-nitroaniline and *m*-phenylenediamine; it is also an intermediate for explosives. It is estimated by reduction to *m*-phenylenediamine by means of stannous chloride and hydrochloric acid, addition of zinc dust to remove tin, and titration with diazotized aniline.

***o*-Dinitrobenzene** (m.p. 118°, b.p. 319°) can be recovered from the preparation of the *m*-compound, if the latter is purified by crystallization.

1,3,5-Trinitrobenzene is best prepared[88] by decarboxylation, effected simply by boiling with water containing a little acetic acid, of trinitrobenzoic acid, obtained by oxidation of trinitrotoluene.

Nitrotoluenes.[89] Mononitration is carried out as in the case of benzene, but the temperature is maintained below 20° to avoid oxidation of the methyl group. A mixture of *o*-, *p*-, and *m*-nitrotoluenes is obtained in the approximate percentages of 63, 35 and 2. On cooling to −10°, part of the *p*-nitrotoluene crystallizes and is separated in a centrifuge. The oil is fractionally distilled under reduced pressure until about 40% has been collected; redistillation gives nearly pure *o*-nitrotoluene. When the still residue is cooled, more of the *p*- separates. In the mononitration of toluene 2-5% of *m*-nitrotoluene is formed, the proportion changing almost linearly[90]



o-
m.p. −9.5°α; −4°β
b.p. 222°

m-
m.p. 16°
b.p. 231°

p-
m.p. 52°
b.p. 238°

Nitrotoluenes

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[6] See p. 50.

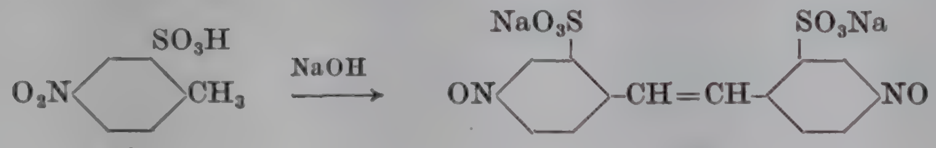
[87] Coward and National Aniline Co., USP 2,040,123.

[88] DRP 77,353; Clarke and Hartman, *OSCV* I, p. 541.

[89] For a complete account of the chemistry and preparation of the nitrotoluenes, see De Beule, *Bull. soc. chim. Belg.* **42,** 27 (1933).

[90] Jones and Russell, *JCS* 921 (**1947**); see also Ingold *et al.*, *ibid.*, 1959 (**1931**).

with temperature between −30° and 60°. This is now carefully recovered from the technical nitration products of toluene by a complex fractional distillation procedure, since *m*-toluidine is a valuable intermediate. A convenient procedure[91] for the preparation of *m*-nitrotoluene in the laboratory is the reduction of diazotized 3-nitro-*p*-toluidine (Fast Red GL Base) with alcohol. The nitrotoluenes are used for reduction to the toluidines; further uses of the *o*-compound are for conversion to *o*-tolidine and *o*-nitrobenzaldehyde, and of the *p*- for sulfonation to 4-nitrotoluene-2-sulfonic acid (I), an intermediate for stilbene dyes. A method (Reverdin and de la Harpe; 1888) for estimating *p*-nitrotoluene in technical *o*-nitrotoluene is based on sulfonation with oleum, followed by treatment with boiling caustic soda solution, when a crimson color develops as a result of the formation of (II), which is unstable, but can be determined colorimetrically. *o*-Nitrotoluenesulfonic acid does not form a stilbene dye by alkali treatment. *p*-Nitrotoluene is more in demand than the *o*-, and IG used[82] the surplus of the latter for further nitration to a mixture of 2,4- and 2,6-dinitrotoluene, which were reduced to the mixed diamines and condensed with phosgene to form the diisocyanates ; polymerization of this mixture gave Desmodur T.[92]



(I) (II)

Dinitration of toluene gives mainly 2,4-dinitrotoluene (m.p. 71°), together with a little of the 2,6-compound which can be separated as an oil when the product is cooled. A method of separation of 2,6-dinitrotoluene (m.p. 66°) is reduction of the mixture in dioxane with hydrogen sulfide and a trace of ammonia, when only the 2,4-compound undergoes reduction and yields 2-nitro-*p*-toluidine.[93] Further nitration of the dinitrotoluenes leads to the well-known explosive TNT. Nitration of *p*-xylene gives only one product, but *m*-xylene gives a mixture of 75% 4-nitro- and 25% 2-nitro-*m*-xylene, which is distilled to remove the 2-nitro isomer. *o*-Xylene on nitration gives a mixture, containing chiefly the 3-nitro- and 4-nitro-*o*-xylenes (55:45) separated by fractionation followed by "sweating."[94] Trinitro-*t*-butyl-*m*-xylene (III), a perfume used under the name of " xylene musk," is made by the action of isobutylene on *m*-xylene at high temperatures in presence of aluminium chloride, followed by trinitration.

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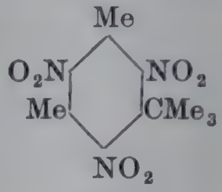
[91] Buchka (1889); Clarke and Taylor, *OSCV* I, p. 415.

[82] See p. 71.

[92] A recent use for various aromatic amines (e.g. 4-chloro-*m*-phenylenediamine, benzidine, 1,5-diaminonaphthalene, triaminotriphenylmethane) is to convert them into the isocyanates (" Desmodurs ") by interaction with phosgene. These isocyanates are useful for tanning leather, application to cellulose for permanent finishes, and polymerization to adhesives and plastics (*BIOS* 719).

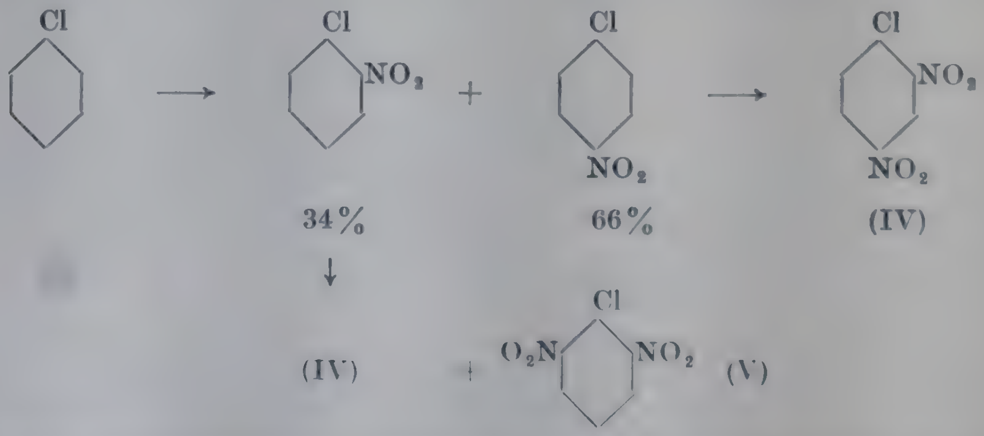
[93] Parkes and Farthing, *JCS* 1275 (**1948**).

[94] *BIOS* **1146**.



(III)

Chloronitrobenzenes. Nitration of chlorobenzene with mixed acid (30% HNO_3 and 56% H_2SO_4) at 40-80° gives a mixture of the *o*- and *p*-compounds (34 and 66%); the *o*:*p* ratio increases slightly with temperature, but is independent of the H_2SO_4/HNO_3 ratio.[95] The isomers are separated somewhat in the same manner as the nitrotoluenes. A first crystallization gives about 40% of the *p*-compound; the eutectic oil is drained off and distilled to yield a product containing about 92% of the *o*-compound. Final purification is effected in crystallizers permitting careful temperature control and slow crystallization. *o*-Chloronitrobenzene melts at 32.5°, and *p*- at 83°. They are used in making the nitrophenols, nitroanisoles, nitrophenetoles, and nitroanilines, and they are also intermediates for sulfur dyes. The dinitration of chlorobenzene is usually carried out without isolation of the mononitro compounds. 1-Chloro-2,6-dinitrobenzene (V; m.p. 88°) is also formed in this manner, and pure 1-chloro-2,4-dinitrobenzene can be obtained by nitrating *p*-nitrochlorobenzene with mixed acid (35% HNO_3, 65% H_2SO_4); the nitration is commenced at 95° and the temperature is reduced later to 45-55°. 1-Chloro-2,4-dinitrobenzene (IV ; yellow rhombic crystals, m.p. 51°, b.p. 315°) is produced on a large scale for conversion into Sulfur Black. The compound crystallizes from ether in two labile forms (β and γ) having m.p. 43° and 27°.[96] Handling must be avoided since it is a powerful skin irritant. The reactivity of the chlorine atom in chlorodinitro-



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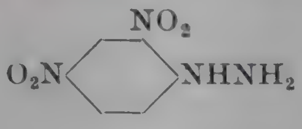
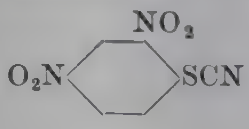
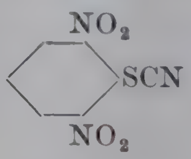
[95] Dey, Govindarajan, and Govindachari, *J. Sci. Ind. Research* (*India*) **3**, 95 (1944).

[96] Hoffman and Dame, *JACS* **41**, 1015 (1919).

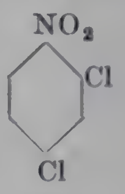
benzene enables it to be used for various condensations, e.g., for the preparation of 2,4-dinitroaniline, -diphenylamine, and -phenylhydrazine. Thus, short refluxing of a solution of chlorodinitrobenzene and hydrazine in alcohol gives an 85% yield of 2,4-dinitrophenylhydrazine (VI; m.p. 197° dec.), a valuable reagent for the characterization of carbonyl compounds.[97]

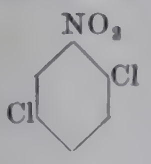

(VI)

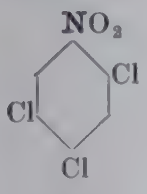

(VII)


(VIII)

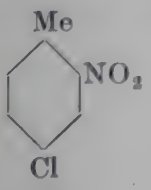
Condensation of crude chlorodinitrobenzene with ammonium thiocyanate in aqueous solution at 80-85° gives the dinitrophenylrhodanates (VII and VIII), which are used in insecticides.[6] *m*-Chloronitrobenzene (m.p. 47·9°, b.p. 236°) is prepared[6] by the chlorination of nitrobenzene in presence of sublimed ferric chloride at 35-40° until the sp. gr. reaches 1·35 at 15°. A crude mixture of the desired compound, nitrobenzene, *o*-chloronitrobenzene, and polychlorinated nitrobenzenes is thus obtained, which has to be purified by fractionation and crystallization (sweating). *m*-Chloronitrobenzene, which is formed to the extent of 0.1-0.2% in the mononitration of chlorobenzene, is also recoverable from the purification of *p*-chloronitrobenzene by heating the fraction rich in the *m*-compound with aqueous caustic soda under pressure at 160°, when the *p*-compound hydrolyzes to *p*-nitrophenol. Nitration of *m*- and *p*-dichlorobenzene gives 2,4-dichloronitrobenzene (IX; m.p. 34°, b.p. 258-259°) and 2,5-dichloronitrobenzene (X; m.p. 56°, b.p. 267°) respectively; and nitration of 1,2,4-trichlorobenzene gives 2,4,5-trichloronitrobenzene (XI; m.p. 57°, b.p. 288°).

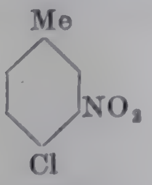

(IX)

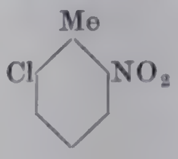

(X)

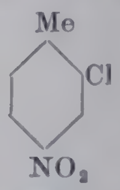

(XI)

Chloronitrotoluenes. Nitration of *p*-chlorotoluene gives a mixture of the 2- and 3-nitro compounds (XII and XIII), which are separated by


(XII)
m.p. 38°;
b.p. 240°/720 mm.


(XIII)
m.p. 7°;
b.p. 260°


(XIV)
m.p. 37°


(XV)
m.p. 68°

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[97] Purgotti (1894); Allen, *OSCV* II, p. 228; Brady, *JCS* 759 (1931).

[6] See p. 50.

fractional distillation and sweating.[6,64] Similar separation of the product of chlorination of *o*-nitrotoluene in presence of ferric chloride gives 4-chloro- and 6-chloro-2-nitrotoluene (XII and XIV).[6] Pure 2-chloro-4-nitrotoluene (XV; m.p. 68°) is obtained[6] by chlorinating *p*-nitrotoluene, and sweating the product, which contains a small amount of 3-chloro-4-nitrotoluene (m.p. 24°, b.p. 146°/19 mm.).

***m*-Bromonitrobenzene** (m.p. 56°) is obtained in 60-75% yield[98] by adding bromine to a mixture of nitrobenzene and iron powder at 135-145°.

α-Nitronaphthalene. Nitration of naphthalene proceeds so readily that better control is obtained and dinitration avoided by using mixed acid of lower concentration than in the case of benzene. Finely powdered naphthalene (1 part) is added in batches alternately with the mixed acid (1.5 parts; composition %: HNO_3 33; H_2SO_4 47.5; H_2O 19.5), to spent acid at 45-55°. The cycle time is about 12 hours. The spent acid is drawn off, and the lumps of nitronaphthalene are washed free from acid and granulated by running the molten substance into water under agitation.[99] The nitro compound may be used without further purification for reduction to the amine (yield 98%). α-Nitronaphthalene crystallizes in long, pale yellow needles, m.p. 57·8°, b.p. 304°, and dissolves in sulfuric acid with a crimson color.

Nitration of naphthalene proceeds almost exclusively in the α-position, although under certain conditions as much as 4-5% of the β-compound is formed,[100] together with traces of dinitronaphthalenes and 2,4-dinitro-1-naphthol. The nitration of tetrahydronaphthalene gives equal parts of the 5- and 6-nitro compounds, which can be fractionated and dehydrogenated by heating with bromine at 100° to α- and β-nitronaphthalenes.[101] β-Nitronaphthalene (plates; m.p. 79°), which is not used as a dye intermediate, can also be prepared from 2-nitro-1-naphthylamine.[102]

When naphthalene or α-nitronaphthalene is nitrated, first at 40° and finally at 80°, with mixed acid in an amount necessary for dinitration, or by means of nitrogen tetroxide,[103] the product is a mixture of 1,5- and 1,8-dinitronaphthalene in a proportion of about 1:2. This mixture is used directly for conversion into Naphthazarin,[104] but must be separated from the resinous material which is formed to the extent of about 25%. Separation, necessary for the preparation of the pure nitronaphthylamines and diaminonaphthalenes, can be effected in various ways, e.g., cooling the nitration product without dilution, or by diluting with hot ethylene dichloride and cooling to 50°, when the 1,5- separates first;[9] using pyridine,[105] concentrated sulfuric acid, aniline,[106] or boiling sodium sulfite solution which dissolves only the 1,8-compound.[107] 1,5-Dinitronaphthalene (yellow needles, m.p. 216°) and the 1,8-isomer (yellow plates, m.p. 173°) form mixed crystals, m.p. 145°, in a proportion of 22:78. All the other eight isomeric dinitronaphthalenes have been prepared by indirect methods, but they are of no technical interest.

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[6] See p. 50.

[64] See p. 65.

[98] Johnson and Gauerke, *OSCV* I, p. 123.

[99] *BIOS* **1143.**

[100] Fierz-David and Sponagel, *Helv. Chim. Acta* **26,** 98 (1943).

[101] Braun *et al., Ber.* **55,** 1678 (1922); Schroeter *et al., Ann.* **426,** 39 (1922); BP 148,923.

[102] Hodgson, Leigh, and Turner, *JCS* 744 (1942).

[103] Schorygin *et al., J. Gen. Chem. U.S.S.R.* **8,** 981 (1938).

[104] See Chapter XXVI.

Nitroanthraquinones. Anthracene nitrates in the *meso*-position, and the reaction has no technical interest. The nitration of anthraquinone requires rather more drastic conditions than in the case of hydrocarbons, heating with mixed acid at 50-75° being necessary. Since the reactivities of the two benzene rings in the anthraquinone molecule are largely independent of each other, exclusive mononitration is not possible, and in fact considerable amounts of 1,5- and 1,8-dinitroanthraquinones are simultaneously formed. Pure α-nitroanthraquinone (m.p. 232.5°, b.p. 270°/7 mm.) is therefore difficult to prepare except by several crystallizations (e.g., from toluene) or by vacuum distillation; boiling the crude nitroanthraquinone with a 1-2% solution of sodium sulfite assists purification.[108] Crude α-nitroanthraquinone can be used for reduction to the amine, but when the purity of the latter is a critical factor, and even from other points of view, a better route to α-aminoanthraquinone is through the sulfonic acid.

Further nitration of α-nitroanthraquinone gives a mixture of 1,5 (m.p. 384-385°, 422°)[5] and 1,8-dinitroanthraquinone (m.p. 312°) from which the former, used for reduction to the 1,5-diamino compound and for the preparation of Anthracene Blue WR, can be separated with relative ease by taking advantage of its sparing solubility in alcohol. Another method of separation is based on the solubility of 1,8-dinitroanthraquinone in monohydrate.[109] It is doubtful, however, if 1,8-dinitroanthraquinone of absolute purity has been obtained so far. Dinitration of anthraquinone in monohydrate gives about 40% of 1,5-, 37% of 1,8-, 12.5% of 1,6-, and some 1,7-dinitroanthraquinones.[110]

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[9] See p. 50.

[105] Finzi, *Ann. chim. applicata* **15,** 55 (1925).

[106] Vorozhtzov and Kulev, *Chem. Abstracts* **23,** 3697 (1929).

[107] Hodgson and Walker, *JCS* 1346 (**1933**); see also Hodgson and Ward, *ibid.* 1109 (**1947**).

[108] Whelen and du Pont, USP 2,302,729.

[5] See p. 50.

[109] *BIOS* **126.**

[110] Hefti, *Helv. Chim. Acta* **14,** 1404 (1931).

β-Nitroanthraquinone (m.p. 185°), which is not formed in the nitration of anthraquinone and is not used as a dye intermediate, can be made from β-aminoanthraquinone (*a*) via the diazonium salt, or (*b*) by nitration to 2-nitro-3-aminoanthraquinone and deamination again via the diazonium salt, or (*c*) by the action of nitrous gases on anthraquinone-β-sulfonic acid in aqueous sulfuric acid solution.[111]

Nitration of 2-methylanthraquinone gives the 1-nitro compound, which may be purified by heating at 90-100° with aqueous sodium sulfite and caustic soda, filtering and washing free from the sodium sulfonates formed.[112] 1-Nitro-2-methylanthraquinone (pale yellow needles, m.p. 269-270°) is a largely used intermediate for the acridone type of anthraquinonoid vat dyes. Its main use is for conversion into 1-nitro- and 1-aminoanthraquinone-2-carboxylic acid. Dinitration leads to a mixture of 1,5-dinitro (m.p. 346-347°), which is the major product, and 1,8-dinitro-2-methylanthraquinone (m.p. 293-294°).

Nitroanthraquinones can be reduced to the corresponding amines by a variety of reagents, sodium sulfide being commonly used. By careful reduction with sodium stannite or glucose or sodium sulfide at a low temperature, the intermediate hydroxylamines ($\text{AQ-NO}_2 \longrightarrow \text{AQ-NHOH}$) can be isolated, and on heating with sulfuric acid they undergo the usual migration of arylhydroxylamines forming 1,4-substituted aminohydroxyanthraquinones. The reaction can be carried out in one operation by heating with sulfur in concentrated sulfuric acid and 1,5-diamino-4,8-dihydroxyanthraquinone can be prepared in this manner from 1,5-dinitroanthraquinone.[113] Nitro groups in the α-position in anthraquinones further undergo a series of characteristic reactions. They can be replaced by sulfonic groups on heating with sodium sulfite solution; by chlorine on passing the gas into a solution of the nitro compound in sulfuric acid; by hydroxyl on heating with aqueous pyridine; by alkylamino and arylamino groups on heating with primary and secondary alkylamines and with primary arylamines; and in certain cases by thiol groups by successive reduction with sodium sulfide under alkaline and under weakly acid conditions. A reaction in which β-nitro groups are more labile than α- is replacement by alkoxyl on heating with caustic potash and alcohol. Some of these reactions are of technical value, and examples will be encountered later. They are also of considerable utility in the laboratory preparation of anthraquinone derivatives in which the substituents are heteronuclear and which are difficult to prepare by other methods. Thus by the sulfonation of nitroanthraquinones and the nitration of anthraquinonesulfonic acids, a series of nitroanthraquinonesulfonic acids can be obtained, which form crystalline and readily separable sodium salts and from which by suitable replacement of the nitro or the sulfonic groups a wide range of anthraquinone derivatives can be obtained. In the nitration of the anthraquinonesulfonic acids, the nitro group enters the α-positions in the unsubstituted ring.

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[111] Datta and Varma, *JACS* **41**, 2048 (1919).

[112] du Pont, USP 2,293,782.

[113] See Chapter XXIX.

The action of oleum on the nitroanthraquinones, usually carried out in presence of sulfur to which boric acid may be added, results in the formation of polyhydroxyanthraquinones and their sulfonic acids.[113]

By the nitration of α-chloro-, 1,5-dichloro-, and 1,8-dichloroanthraquinones, substitution takes place in α-positions. Thus the products are 1-chloro-4-nitro-, 1,5-dichloro-4-nitro- and 4,8-dinitro, and 1,8-dichloro-4-nitro- and 4,5-dinitroanthraquinone.

AMINATION

The main method, both in the laboratory and in technical practice, for the introduction of an amino group into an aromatic compound, is nitration and reduction. Iron in presence of a little hydrochloric acid is the common reducing agent, and hundreds of tons of cast iron borings, collected as a by-product from machine manufacturing industries, are used for this purpose in the production of dyestuff intermediates. Zinc, tin and stannous chloride are frequently employed in the laboratory. Reduction by means of hydrogen in presence of copper or nickel catalyst has been successfully employed, e.g., for nitrobenzene and α-nitronaphthalene. The reduction of nitrophenols and nitroanthraquinones and the partial reduction of *m*-dinitrobenzene are effected by sodium sulfide. Sodium bisulfite solution under pressure is sometimes used, sulfonation being effected simultaneously (e.g., α-nitronaphthalene ⟶ 1-naphthylamine-2,4-disulfonic acid). Electrolytic reduction has been studied, but is of no value for the conversion of nitro compounds to the corresponding amines. The reduction of an azo compound ($\text{Ar–N=N–Ar}' \longrightarrow \text{ArNH}_2 + \text{Ar}'\text{NH}_2$), e.g., by means of alkali and sodium hydrosulfite, is useful for the preparation of certain complex monamines or simple diamines. An example of a primary amine prepared by reduction of a nitroso compound is *p*-aminodimethylaniline obtained by the action of zinc dust on *p*-nitrosodimethylaniline.

The replacement of a chlorine atom by the amino group ($\text{ArCl} + \text{NH}_3 \longrightarrow \text{ArNH}_2 + \text{HCl}$) is an important method. Chlorobenzene requires high temperature and pressure and a copper catalyst, while a lower pressure in the absence of copper is adequate for the amination of *p*-chloronitrobenzene, and the replacement proceeds at ordinary pressure with 1-chloro-2,4-dinitrobenzene owing to the effect of the nitro groups on the lability of the chlorine atom. An α-chlorine atom in anthraquinone and its derivatives can be replaced by interaction with *p*-toluenesulfonamide in nitrobenzene solution in presence of potassium carbonate and a copper salt, followed by hydrolysis of the anthraquinonylamide by concentrated sulfuric acid ($\mathrm{AQ{-}Cl + ArSO_2NH_2 \xrightarrow{Cu} AQ{-}NH{-}SO_2Ar \xrightarrow{H_2SO_4} AQ{-}NH_2 + ArSO_3H}$). In the anthraquinone series the amines are conveniently prepared by the action of ammonia under pressure on the sodium sulfonates ($\mathrm{AQ{-}SO_3Na + NH_3 \longrightarrow AQ{-}NH_2 + NaHSO_3}$). The Bucherer reaction,[114, 115] used mainly in the naphthalene series, consists in heating a hydroxy compound with ammonium sulfite and ammonia under pressure. When excess of these reagents is used, the reaction proceeds in one stage ($\mathrm{Ar{-}OH + NH_3 \longrightarrow Ar{-}NH_2}$). Sodium sulfite or bisulfite and ammonia can also be used, and the first stage then is the formation of a sodium aryl sulfite ($\mathrm{Ar{-}OH + Na_2SO_3 \longrightarrow Ar{-}O{-}SO_2Na + NaOH}$; $\mathrm{ArOH + NaHSO_3 \longrightarrow Ar{-}O{-}SO_2Na + H_2O}$) or of a bisulfite addition compound with the naphthol in the tautomeric ketone form. Both stages of the reaction are reversible, and excess of ammonia must be present to enable it to proceed to completion in the desired direction; the reverse reaction, also named after Bucherer, is in fact utilizable for the preparation of naphthols from naphthylamines. The Bucherer synthesis of amines is not applicable to phenol, but resorcinol can be converted in excellent yield to *m*-aminophenol. While the reaction is invaluable for the preparation of β-naphthylamine and naphthylamine derivatives in general, α-naphthol derivatives with a sulfonic group in the 2- or 8-position and β-naphthol derivatives with a sulfonic group in the 4-position will not react. A particularly useful feature of the Bucherer reaction is the fact that ammonia can be replaced by both aliphatic and aromatic amines, so that secondary amines such as *N*-methyl- and *N*-phenylnaphthylamines can be prepared. When a dihydroxynaphthalene is heated with ammonia or a primary amine, and if one hydroxyl is in an α-position and the other β-, the β-hydroxyl is preferentially replaced; thus 1,7-dihydroxynaphthalene gives 7-amino-1-naphthol. A modification of the Bucherer amine synthesis is to heat a phenol with ammonia in presence of zinc chloride, ferric chloride, aluminium hydroxide,[116] or

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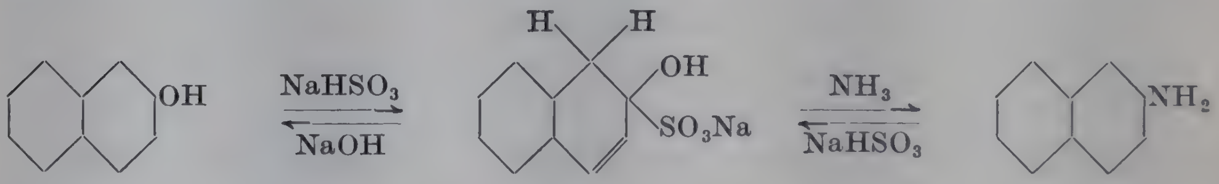
[113] See p. 78.



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[114] *J. prakt. Chem.* (ii), **69**, 43; **70**, 345 (1904).

[115] The Bucherer reaction has been reviewed by Drake, Organic Reactions, I. Wiley, New York, 1942, p. 105-128.

[116] ICI, BP 355,715; IG, BP 368,373; Birch *et al.*, BP 619,877.

ammonium chloride; thus *m*-cresol, heated with ammonium chloride at 350° under pressure, gives 35% of *m*-toluidine and of di-*m*-tolylamine.[117]

The mechanism of the Bucherer reaction has been the subject of a recent kinetic study by Cowdrey and Hinshelwood.[118] Naphthionic and Laurent's acids react bimolecularly with HSO_3^-. The probable mechanism involves as the rate-determining step the 1,2-addition of HSO_3^- at the double bond adjacent to the amino or substituted amino group. The hydrolytic end products are the corresponding naphthols. The effect of changing pH on the rates indicates a reaction of the two negative ions, HSO_3^- and $C_{10}H_6(NH_2)SO_3^-$. The intermediate addition products of the reaction of HSO_3^- and naphthionic acid have been isolated. The major product is probably a dimeric dibisulfite. The reactions of sodium 1-naphthol-4- and -5-sulfonates with HSO_3^- to form the corresponding dibisulfite complexes are reversible. The forward reaction is bimolecular, while the complexes dissociate unimolecularly. On the basis of all the results including the kinetics of the conversion of naphthols to naphthylamines, the mechanisms correspond to the reversible addition and removal of HSO_3^- at the double bond adjacent to OH or NH_2, followed by reversible substitution of OH or NH_2 by each other. The rate-determining step of the overall reaction is the reversible addition of HSO_3^- to the double bond.

Heterocyclic compounds, such as pyridine and quinoline, are aminated in the α-position by the action of sodamide.[119, 120] β-Naphthol can be converted into 5-amino-2-naphthol by heating with sodamide in naphthalene at 200°.[121] Nitro compounds (e.g., α-nitronaphthalene) yield the *p*-amino derivatives (e.g., 4-nitro-1-naphthylamine) by heating with hydroxylamine and alcoholic caustic potash.[122]

Aniline. In the reduction of nitrobenzene by means of iron and hydrochloric acid, the amount of acid employed is only a very small fraction of the stoichiometric quantity in the equation: $PhNO_2 + 3Fe + 6HCl \longrightarrow PhNH_2 + 3FeCl_2 + 2H_2O$; and the reaction proceeds essentially according to the equation : $4PhNO_2 + 9Fe + 4H_2O \longrightarrow 4PhNH_2 + 3Fe_3O_4$. The reduction of nitrobenzene to aniline is an exothermic reaction: $PhNO_2 + 6H \longrightarrow PhNH_2 + 2H_2O + 238{,}000$B.t.u. per pound-mole at 20°. A mixture of nitrobenzene, water and a little hydrochloric acid (or ferrous chloride) is heated by direct steam in a cast-iron still fitted with a powerful "heavy duty" agitator, reflux as well as distillation heads, and an inlet for the addition of iron borings by an automatic device. Steam is then shut off and iron powder added in small portions during several hours at such a rate that the heat of reaction keeps the liquid in ebullition, but the reaction must not be allowed to become too vigorous to avoid the reduction of aniline to benzene. Aniline is then isolated from the iron sludge and water, after neutralization with chalk, by steam distillation or direct vacuum distillation of the entire mixture; or the iron oxide can be removed by filtration, the aniline layer separated and distilled in vacuo. Aniline is soluble in water to the extent of about 3%, and the aqueous layers are therefore returned to the process or extracted with nitrobenzene. The total yield is about 97%.

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[117] Morgan and Pratt, *J. Soc. Chem. Ind.* **51,** 283T (1932).

[118] Cowdrey and Hinshelwood, *JCS* 1036 (**1946**); see, however, Ufimtsev, *Chem. Abstracts* **42,** 6782 (1948).

[119] Tschitschibabin and Seide, *J. Russ. Phys. Chem. Soc.* **46,** 1216 (1914). The amination of heterocyclic bases by alkali amides has been reviewed by Leffler, Organic Reactions, I, Wiley, New York, 1942, p. 91-104.

[120] The preparation and grinding of sodamide, which is highly explosive on slight exposure to the atmosphere and therefore has to be carefully handled, and the preparation of 2-amino- and 2,6-diaminopyridine in a steel ball mill, have been described by Shreve *et al.*, *Ind. Eng. Chem.* **32,** 173 (1940); See also Bergstrom, *Org. Syntheses* **20,** 86 (1940).

[121] Sachs, DRP 173,522; 181,333; *Ber.* **39,** 3014 (1906).

[122] Goldhahn, *J. prakt. Chem.* **156,** 315 (1940); Price and Voong, *Org. Syntheses* **28,** 80 (1948). See also Turski, BP 626,661.

When modified conditions of reduction (e.g., the addition of aluminium or other metal chlorides; increase of the concentration of hydrochloric acid; use of ferrous chloride and a little sulfuric acid) are employed, the ferrous oxide is in a suitable form for conversion by roasting at a suitable temperature into yellow, red, violet, and black pigments for the paint and varnish industries.[76, 123]

Aniline can be obtained in 99% yield by the reduction of nitrobenzene with hydrogen in presence of reduced copper chromate as catalyst.[124] There are several patents on the vapor phase reduction of nitrobenzene by hydrogen in presence of copper, nickel, platinum, and other catalysts.[125] Using a copper catalyst, a yield of about 98% can be obtained, and IG at Ludwigshafen were making about 300 tons per month of aniline by this method.[6, 126] The catalyst consisted of basic copper carbonate and sodium silicate on pumice. The reduction was carried out in a series of two converters. The reaction began at 170° in the first converter, and it rose to 350° in the second on account of the heat of formation of aniline from nitrobenzene. As the catalyst became older, these temperatures increased to 280–460°.

In the Dow process for the manufacture of aniline, chlorobenzene is heated with four to five times the theoretical amount of 25–30% aqueous ammonia in presence of copper at about 240° and about 2,000 lbs. pressure;

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[76] See p. 69.

[123] The mechanism of formation of iron oxides with different compositions and colors during the reduction of nitrobenzene with iron has been investigated by Riskin, *J. Applied Chem.* (*U.S.S.R.*) **19**, 569 (1946).

[124] Doyal and Brown, *J. Phys. Chem.*, **36**, 1549 (1932).

[125] E.g., MLB, DRP 282,492.

[6] See p. 50.

[126] *FIAT* 649.

the reuse of the cuprous oxide sludge, which is in a super-reduced and highly active form, is an advantage.[127] Both batch and continuous processes can be employed. Some phenol is formed as a by-product and is recovered by washing with alkali. If excessive temperature and pressure are used, diphenylamine is also formed.

Aniline vapors are toxic. Pure aniline is a colorless oil, b.p. 184°, m.p. −6.2°, d_4^{15} 1.026. It rapidly darkens in color on keeping, if aminothiophenes are present. Tests for the purity of aniline include determination of moisture and of the freezing point, and examination for the presence of nitrobenzene and of sulfur compounds. Two methods are available for quantitative estimation. Aniline forms a tribromo compound on the addition of potassium bromide-bromate and acid, and the excess of bromine is determined in the usual manner. The ready trichlorination and tribromination of aniline offers a convenient method for the preparation of symmetrical trichloro- and tribromobenzene by diazotization and reduction with alcohol.[128] A general method for the estimation of readily diazotizable aromatic primary amines is titration in acid solution with sodium nitrite, using starch-iodide paper for noting the end point.

Aniline is so largely used as an intermediate that coal-tar dyes in general were known at one time as aniline dyes. Aniline hydrochloride (" aniline salt ") is used in large quantities for oxidation to aniline black on the fiber. Among the dyes in the preparation of which aniline is used are azo, triphenylmethane, and azine dyes and indigo; aniline is also useful as a reagent for the phenylation of amines.

The chloro and dichloroanilines are largely used intermediates for azo dyes, and they are all prepared by the reduction of the corresponding nitro compounds with iron and water in presence of hydrochloric acid or formic acid. *o*- and *m*-Chloroaniline (b.p. 209°; 236°) and 2,5-dichloroaniline (m.p. 50°, b.p. 251°) are used in azoic dyeing as Fast Bases (Fast Yellow G, Fast Orange G, and Fast Scarlet GG Bases respectively).[129] *p*-Chloroaniline (m.p. 70°, b.p. 231°) is manufactured on a considerable scale, while 2,4-dichloroaniline (m.p. 63°, b.p. 245°), 3,4-dichloroaniline (m.p. 71.5°, b.p. 272°) and 2,4,5-trichloroaniline (m.p. 96.5°) are minor products.

Toluidines are made by the iron-acid reduction of the corresponding nitro compounds. All the three are intermediates for azo dyes. *o*-Toluidine (colorless oil, b.p. 199°) and *p*-toluidine (colorless plates; m.p. 45°, b.p. 200.4°) are also used for triphenylmethane dyes, and the *p*-compound for Primuline and acid dyes of the anthraquinone series.

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[127] Hale, Britton, and Williams, USP 1,607,824; 1,726,170-3; 1,775,360; 1,764,869; 1,804,466; 1,840,760; 1,932,518; 2,028,065.

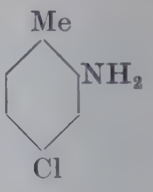
[128] Jackson and Moore (1890); Coleman and Talbot, *OSCV* II, p. 592.

[129] See Chapter XXII.

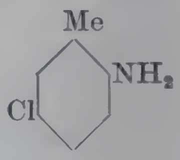
Commercial *p*-toluidine is usually pure and free from the isomers, but *o*-toluidine may contain about 1% of the *p*-isomer. When the amount of *p*- in *o*- is less than 10%, it can be estimated by a colorimetric method (Schoen) based on the fact that oxidation with dichromate and acid gives a red solution, the intensity of which depends on the amount of *p*-toluidine, since the latter is necessary for the formation of a triphenylmethane dye.[130] Schoen's colorimetric method is only approximate and is only applicable to a mixture of high *p*-content. For mixtures of low *p*-content, a known quantity of pure *p*-toluidine can be added and the setting point of this mixture compared with a setting point-composition diagram.[131] *p*-Toluidine in a mixture of the three toluidines can be estimated by the nitrogen evolved when the diazonium salts are decomposed under standard conditions, *p*-toluenediazonium chloride being much more stable than the two isomers.[132]

m-Toluidine (b.p. 203°) is valuable as a middle component in the preparation of disazo and polyazo dyes; and an interesting use is the preparation of pure *m*-cresol via the diazonium salt. *m*-Toluidine in a mixture of the toluidines can be estimated by bromination with potassium bromide and bromate solutions and determination of the excess of bromide-bromate; three atoms of bromine are taken up by *m*-toluidine, and only two by the *o*- and *p*-compounds.[131]

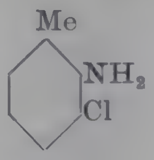
4-Chloro-*o*-toluidine (I; m.p. 21–2°, b.p. 237°/722 mm.) and 5-chloro-*o*-toluidine (II; m.p. 29–30°, b.p. 236–238°/730 mm.), especially the latter, are important intermediates used in azoic dyeing[129] as hydrochlorides under the respective names of Fast Red KB Base and Fast Red TR Base The former base (I) is prepared by iron and aqueous formic acid reduction of the corresponding nitro compound. 5-Chloro-*o*-toluidine (II) is prepared[6] by chlorination of acet-*o*-toluidide in chlorobenzene solution below 50°. Hydrogen chloride is stripped by heating to 130°, the residue neutralized with caustic soda solution, and chlorobenzene recovered by steam distillation. Hydrolysis of the acetyl group is then effected by treatment with 33% caustic soda solution at 175° in an autoclave for 8 hours. On dilution the lower layer of (II) and 3-chloro-*o*-toluidine (III), formed as a by-product in the



(I)



(II)



(III)

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[130] See Chapter XXIII.

[131] Evers and Strafford, *J. Soc. Chem. Ind.* **46,** 114T (1927).

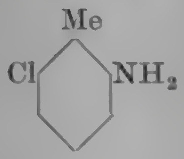
[132] Benbrook and Kienle, *Ind. Eng. Chem. Anal. Ed.* **14,** 427 (1942).

[129] See p. 83.

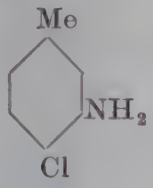
[6] See p. 50.

chlorination, is separated. After a predistillation under vacuum to remove nonvolatile tar, the bases are separated by fractional distillation, the 5- and 3-chloro compounds being obtained in yields of about 68 and 9% respectively. The entire process must be carried out in specially designed plant on account of the extreme toxicity of 5-chloro-*o*-toluidine, the vapors of which produce acute hemorrhagic cystitis. The base is finally converted into the hydrochloride by passing hydrogen chloride into a solution in methylene chloride or chloroform.

6-Chloro-*o*-toluidine (IV; b.p. 245°) and 4-chloro-*m*-toluidine (V; m.p. 29–30°, b.p. 230°) are prepared by the iron reduction of the corresponding nitro compounds.

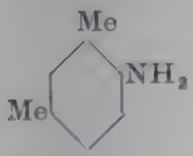


(IV)

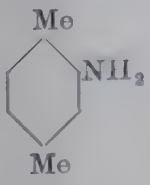


(V)

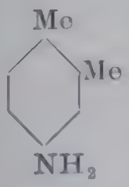
Xylidines are prepared by nitration and reduction of the three xylenes in admixture. The mixed xylidines are useful as blending agents in aviation gasolines to extend supplies and to improve antiknock performance. Their preparation for this purpose by high-pressure catalytic hydrogenation of nitroxylenes, obtained by mononitration of the by-product xylenes recovered from the production of toluene from petroleum by the hydroforming process, has been described recently.[133] In mononitro compounds which are to be reduced catalytically, the presence of dinitro compounds is undesirable since they offer a serious explosion hazard; a method of removal is to treat the dinitro compound with sodium sulfide and extract with acid the nitroamino compound thus formed.[134] Two of the xylidines are mainly useful as dye intermediates: *m*-4-xylidine (VI; b.p. 215.8–216.0°/728 mm.) for scarlet azo dyes and *p*-2-xylidine (VII; m.p. 15.5°, b.p. 213.5°) for aminoazo compounds. *o*-4-Xylidine (VIII; m.p. 51°, b.p. 226°) is important as an intermediate used in the synthesis of riboflavin (lactoflavin; vitamin B_2). When glacial acetic acid is added to the mixed xylidines, (VI) crystallizes as the acetate; when this is separated and hydrochloric acid is added to the



(VI)



(VII)



(VIII)

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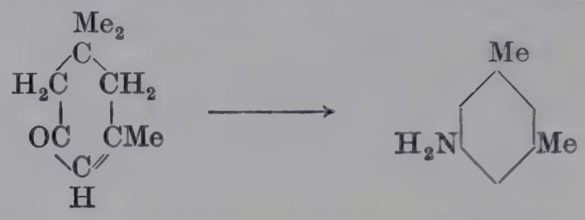
[133] Kunc, Jr., Brown, Voorhies, Jr., *et al.*, *Ind. Eng. Chem.* **40**, 1530, 1538, 1543 (1948).

[134] Gage, USP 2,430,421.

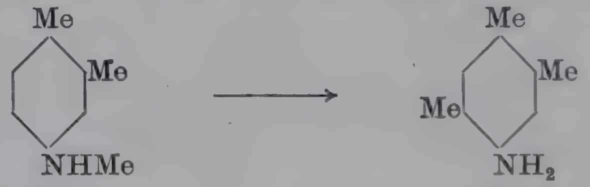
filtrate, *p*-xylidine hydrochloride crystallizes.[134a] The xylidines can also be prepared by reduction of the pure nitroxylenes described earlier. Dimethylaniline, passed over an acid-activated catalyst, such as a mixture of a natural aluminium silicate and 10% of phosphotungstic acid, at 200° yields *m*-4-xylidine.[135] *m*-5-Xylidine (IX; b.p. 220–221°) has been obtained in 60% yield by treating isophorone with excess ammonia at 400–650° in presence of a dehydrogenation catalyst such as chromium, cobalt, or nickel on alumina.[136]

Isophorone



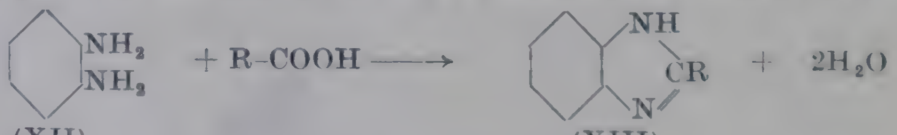
(IX)

Pseudocumidine (XI) is prepared by an interesting method. When a xylidine (e.g., VIII) is heated with methanol and hydrochloric acid under pressure, the *N*-methyl compound (X) first formed isomerizes to (XI), m.p. 62°, isolable as the sparingly soluble nitrate. The mixed xylidines obtained as a residue after removal of (VI) and (VII) are suitable as raw material for this reaction.



(X) (XI)

***o*-Phenylenediamine** (XII; m.p. 103°, b.p. 257°) is prepared by heating *o*-nitroaniline with about 12 times its weight of 17% sodium sulfide solution at 105° in an autoclave for a few hours. The diamine is obtained in 97–99% purity and 84% yield.[10] The reduction of *o*-nitroaniline can be carried out in the laboratory with zinc dust and alcoholic caustic soda.[137] *o*-Diamines undergo several characteristic cyclizations; thus they condense with 1,2-diketones (e.g., phenanthraquinone) to form quinoxalines. *o*-Phenylenediamine is useful as a reagent for characterization of aliphatic acids, with which it forms 2-alkylbenzimidazoles (XIII).[138]



(XII) (XIII)

[134a] Cf. Anglo-Iranian Oil Co., BP 619,873.

[135] IG, BP 421,791.

[136] Shell Development Co., BP 586,518.

[10] See p. 50.

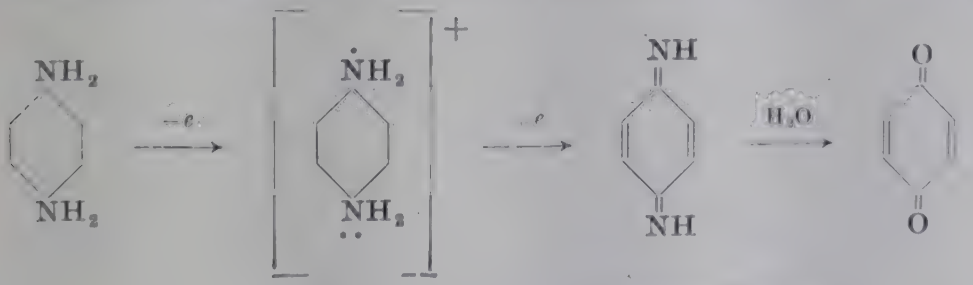
[137] Hinsberg and Koenig (1895); Martin, *OSCV* II, p. 501.

[138] Seka and Mueller, *Monatsh.* 57, 97 (1931); Wagner and Millett, *OSCV* II, p. 65.

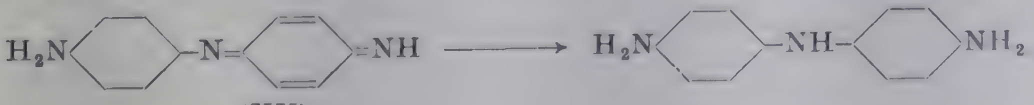
m-Phenylenediamine (m.p. 63°, b.p. 287°) is prepared by reduction of *m*-dinitrobenzene in the same manner as aniline from nitrobenzene; the reaction is very vigorous and is controlled by slow addition of the nitro compound to hot water and iron. Completion of the reaction is indicated by a spot on filter paper being colorless and not yellow. The mixture is made alkaline with soda ash, boiled, filtered, and the iron oxide residue extracted once or twice with boiling water. The diamine solution can be used directly for the preparation of azo dyes, or it can be isolated as the hydrochloride. Purification of the base, if necessary, is effected by vacuum distillation. The colorless crystals of the diamine rapidly darken in color with development of an odor of ammonia. *m*-Phenylenediamine is estimated by titration with diazotized aniline to form Chrysoidine, and a characteristic reaction is the formation of Bismarck Brown on treatment with nitrous acid.

m-Toluylenediamine (m.p. 99°) is made[139] by reduction of 2,4-dinitrotoluene, and like *m*-phenylenediamine it is used for making azo dyes.

p-Phenylenediamine (colorless needles, m.p. 147°, b.p. 267°). This amine is made technically by the reduction of *p*-nitroaniline. Reduction of *p*-aminoazobenzene and amination of *p*-dichlorobenzene are possible methods. The *p*-diamine, which is more stable than the *m*-compound, is purified by vacuum distillation. *p*-Phenylenediamine is characterized by its ready convertibility to quinone by oxidation. The intensely colored intermediate products of the oxidation of *p*-phenylenediamine and its derivatives, called Wurster's salts, exist as free radicals (semiquinones) in dilute solution and as dimers or higher polymers in higher concentration. These semiquinones (e.g., XIV) are much more stable than the corresponding fully oxidized quinonediimines and quinoneimines, which are readily hydrolyzed to the quinones.[140] A blue indamine (XV) is formed when *p*-phenylenediamine is oxidized in admixture with a primary amine



(XIV) *p*-Quinonediimine



(XV)

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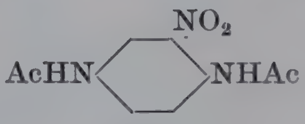
[139] Hofmann (1861); Mahood and Schaffner, *OSCV* II, p. 160.

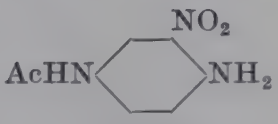
[140] Weissberger *et al.*, *JACS* **70**, 2223 (1948); and earlier papers; Michaelis *et al.*, *ibid.* **65**, 1747 (1943) and earlier papers.

unsubstituted in the *p*-position. Indamines are intermediates for Safranine dyes.[141] Reduction of the indamine (XV) gives 4,4′-diaminodiphenylamine, an intermediate for disazo dyes. *p*-Phenylenediamine is also used for dyeing hair and fur and for making sulfur dyes.

***p*-Aminoacetanilide** (m.p. 162°) is made by the iron and hydrochloric acid or zinc dust and acetic acid reduction of *p*-nitroacetanilide, prepared by nitration of acetanilide. When it is acetylated to form *N*,*N*-diacetyl-*p*-phenylenediamine and nitrated, the product is (XVI). Hydrolysis of (XVI) with 2% caustic soda solution at 100° for 30 minutes results in partial deacetylation to 3-nitro-4-aminoacetanilide (XVII; red needles, m.p. 189°).


NO2
AcHN
NHAc

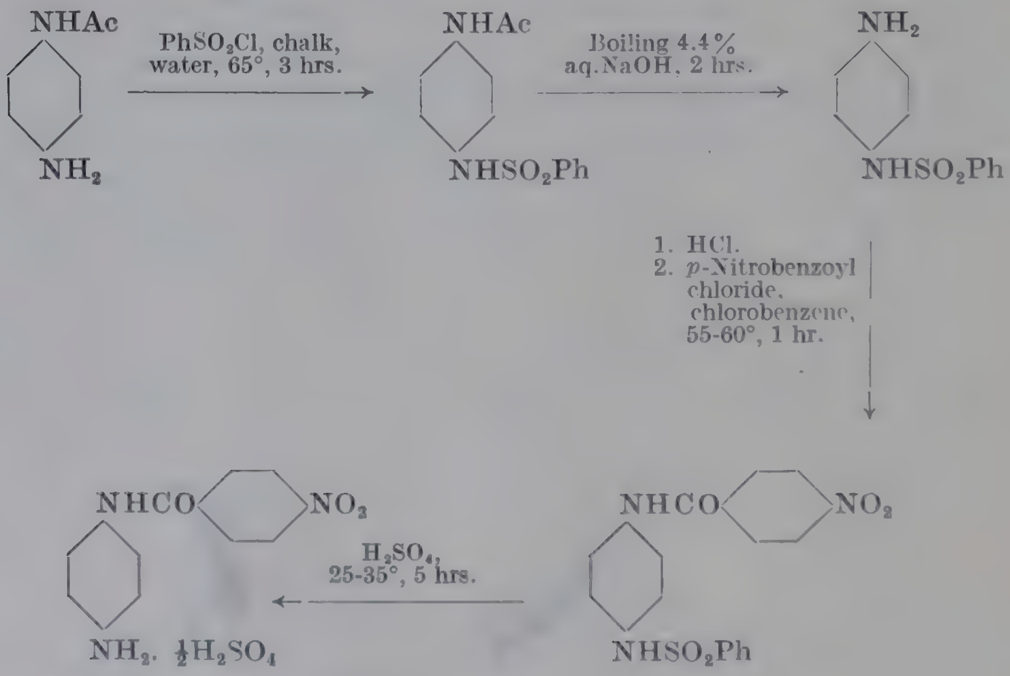
(XVI)


NO2
AcHN
NH2

(XVII)

Mono-*p*-nitrobenzoyl-*p*-phenylenediamine (XVIII) is prepared[10] by an interesting series of reactions (Chart 4) based on the relative ease of hydrolysis of *N*-acetyl, *N*-arylsulfonyl and *N*-benzoyl groups.

CHART 4


NHAc
NH2
PhSO2Cl, chalk, water, 65°, 3 hrs.
NHAc
NHSO2Ph
Boiling 4.4% aq.NaOH, 2 hrs.
NH2
NHSO2Ph
1. HCl.
2. p-Nitrobenzoyl chloride, chlorobenzene, 55-60°, 1 hr.
NHCO
NO2
NHSO2Ph
H2SO4, 25-35°, 5 hrs.
NHCO
NO2
NH2. ½H2SO4

(XVIII)

p-Toluylenediamine (XIX; m.p. 64°, b.p. 274°) is obtained by reduction of aminoazotoluene (XX), and in its properties and uses it is similar to *p*-phenylenediamine.

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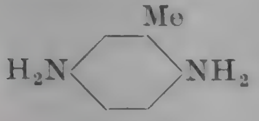
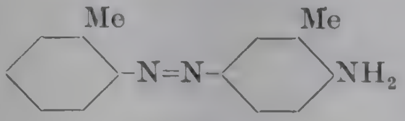
[10] See p. 50.

[141] See Chapter XXV.

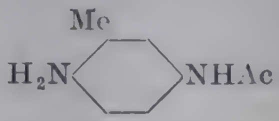
6-Amino-acet-m-toluidide (XXI), a minor intermediate for the preparation of azo dyes, is obtained from acet-*m*-toluidide by nitration and reduction. During the nitration about 8% of the 4-nitro isomer is formed, but this is not separated.[10]



(XIX)



(XX)



(XXI)

α-Naphthylamine (colorless needles or prisms, m.p. 49.3°, b.p. 301°) is manufactured[99] by reduction of the nitro compound with iron and acid (or ferrous chloride); reduction by means of hydrogen in presence of a nickel or copper catalyst can also be conveniently employed.[142] A yield of about 98% is obtainable by either method. The amination of α-chloronaphthalene with ammonia and a copper catalyst has been described.[143] After reduction of nitronaphthalene with iron and acid, the amine is isolated by extraction with benzene. The product contains a little β-naphthylamine, and is purified by vacuum distillation or by melting with 10% of its weight of ligroin and cooling, when the pure α-compound can be separated by centrifugation. The naphthylamines, especially the β-isomer, are carcinogenic, and the plant must be so designed and operated that handling is avoided. Although the freezing point of pure α-naphthylamine is 48.61–48.63°, commercial α-naphthylamine has f.p. 45.3–45.5° and is not more than 95.5% pure; an invariable impurity is the β-compound.[144] On exposure to air the color gradually changes to greyish violet, probably owing to the presence of 1,8-diaminonaphthalene. Its main use is in making azo dyes; under the name Fast Garnet B Base it was used at one time in azoic dyeing. α-Naphthylthiourea (" ANTU ") is a rodenticide.

β-Naphthylamine is made in nearly quantitative yield by the Bucherer reaction, in which a mixture of β-naphthol (114 parts), 22% ammonium sulfite solution (600 parts) and 20% ammonia (125 parts) is heated under pressure and with stirring in an autoclave at 105° for 8 hours.[145, 5] In an alternate procedure β-naphthol (1 part), 28% ammonia (16 parts), and sulfur dioxide (0.15 part) are heated at 185° for 18 hours.[146] After cooling the amine is collected on a closed filter, washed with aqueous caustic soda to remove β-naphthol, and purified by vacuum distillation. The still residues contain the much higher boiling 2,2′-dinaphthylamine, the formation of which is unavoidable. A 95% yield of β-naphthylamine can be obtained by passage of β-naphthol and ammonia over alumina at 430–450°.[147] β-Naphthylamine crystallizes in colorless plates, m.p. 112°, b.p. 306°; it turns pink in color on storage. The purity (about 98–99%) of commercial β-naphthylamine can be estimated by titration with sodium nitrite solution.[148] Unlike the α-compound, which has a characteristic disagreeable smell, β-naphthylamine is odorless. Its main use in the dyestuff industry is for conversion into γ- and J-acids; *N*-phenyl-β-naphthylamine is used as an antioxidant in the rubber, oil, and soap industries.

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[10] See p. 50.

[99] See p. 76.

[142] Parrett and Lowy, *JACS* **48**, 778 (1926).

[143] Groggins and Stirton, *Ind. Eng. Chem.* **28**, 1051 (1936).

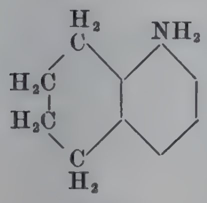
[144] Gubelmann and Weiland, *ibid.* **21**, 1239 (1929).

[145] BASF, DRP 117,471; Bucherer, *J. prakt. Chem.* (ii) **69**, 88 (1904).

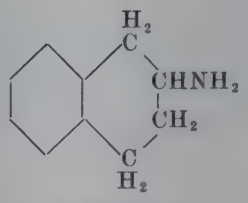
[5] See p. 50.

[146] *CIOS* Item 22, File XXIX–14.

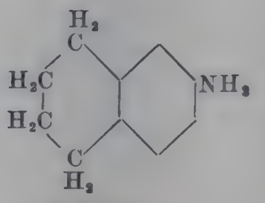
The two naphthylamines behave differently on reduction with sodium and amyl alcohol or on catalytic hydrogenation. α-Naphthylamine gives *ar*-tetrahydro-α-naphthylamine (XXII) as the main or sole product in all cases. The product from β-naphthylamine varies with the reducing agent. Sodium and alcohol gives mainly the *ac*-compound (XXIII);[149] catalytic reduction under certain conditions gives about 75% of the *ar*-amine (XXIV) and under other conditions (XXIII).[150] The *ar*-amines (XXII) and (XXIV) can be prepared by the reduction of the nitro compounds obtained by nitration of tetralin as mentioned earlier. Azo dyes[151] are obtained in the normal manner from (XXII), whereas (XXIV) forms diazoamino compounds and not azo dyes by coupling with diazonium salts.[152]



(XXII)
b.p. 275°/712 mm.



(XXIII)
b.p. 249°/710 mm.
(dec.)



(XXIV)
m.p. 38°;
b.p. 275–7°/713 mm.

All ten possible diaminonaphthalenes have been prepared, but they are not used as dye intermediates. Their interest in dyestuff chemistry is in connection with the identification of azo dyes. Thus 1,2- and 1,4-diaminonaphthalenes are obtained when 1-amino-2-azo (or 2-amino-1-azo) and 1-amino-4-azo dyes are reduced. 1,2-Diaminonaphthalene (m.p. 98°) can be conveniently prepared by hydrogenation of 1-benzeneazo-2-naphthylamine in alcohol with Raney nickel at room temperature and about 40 lbs.

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[147] Howald and Lowy, USP 1,449,423; *Ind. Eng. Chem.* **15,** 397 (1923).

[148] Lee and Jones, *ibid.* **14,** 961 (1922).

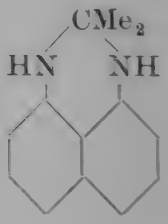
[149] Waser and Möllering, *OSCV* I, p. 499.

[150] IG, BP 290,175; ICI, BP 506,928; Wulff and IG, DRP 581,831; Adkins and Cramer, *JACS* **52,** 4349 (1930).

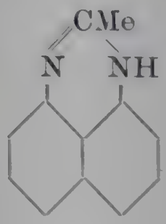
[151] For an account of their properties, see Rowe, *J. Soc. Dyers Colourists* **35,** 128 (1919); **41,** 5 (1925).

[152] Smith, *JCS* **81,** 900 (1902).

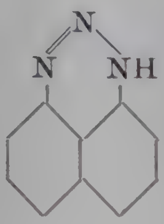
pressure. 1,5-Diaminonaphthalene (m.p. 190°), readily obtainable from 1,5-dinitronaphthalene, was used at one time as an intermediate for disazo dyes. The 1,8-diamine (m.p. 66.5°), similarly prepared, is interesting as a peri-compound which can undergo various condensations leading to colored or colorless heterocyclic derivatives, depending on the presence or absence of a double bond in the heterocyclic ring.[153] Examples are (XXV), (XXVI), and (XXVII); (XXVI), produced in 83% yield by treating an aqueous solution of 1,8-diaminonaphthalene hydrochloride with acetic anhydride at 30-40°, is a useful dye intermediate.[9] "Phthaloperinone" (XXVIII), obtained by reaction of the diamine with phthalic anhydride at 240°, was used by the Germans during the war for producing orange colored smokes. 1,8-Diaminonaphthalene has been mentioned as a rubber preservative.[154]



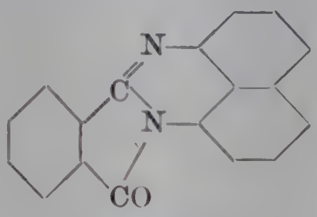
(XXV)
Colorless



(XXVI)
Green



(XXVII)
Red



(XXVIII)

AMINOANTHRAQUINONES

The greater lability of substituent groups in anthraquinones in comparison with those in similar compounds of the benzene and naphthalene series provides several methods by which aminoanthraquinones and their derivatives can be prepared. (1) α-Aminoanthraquinones can be prepared by reduction of the nitro compounds with boiling sodium sulfide solution. The method is more useful for the preparation of derivatives of 1-aminoanthraquinone (e.g., 1-amino-2-methylanthraquinone and 1-amino-4-methoxyanthraquinone) than for the parent amine. (2) Sulfonic acids are heated with ammonia in presence of an oxidizing agent ($AQ\text{-}SO_3H + 3NH_3 + O \longrightarrow AQ\text{-}NH_2 + (NH_4)_2SO_4$).[155] (3) A chloroanthraquinone is heated with ammonia at about 200°, the addition of a copper salt or an oxidizing agent being advantageous. Chlorine in the α-position is more labile than in the β-position; and 1-chloroanthraquinone with a sulfonic group in the 5-, 6-, 7-, or 8-position reacts smoothly at 100° to give the corresponding

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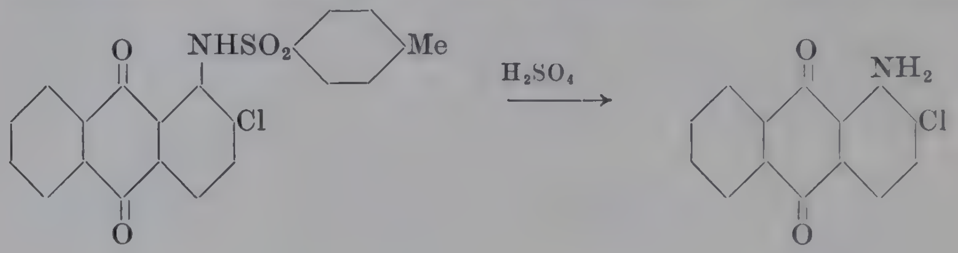
[153] Sachs, *Ann.* **365,** 53 (1909).

[9] See p. 50.

[154] Geer and Jones, USP 1,532,398.

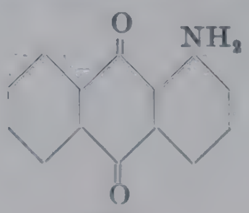
[155] Lauer, *J. prakt. Chem.* (ii) **135,** 7 (1932); DRP 480,848; USP 1,933,236; Bamberger and Allied Chemical and Dyestuff, USP 2,443,885.

1-aminoanthraquinonesulfonic acid. (4) A general method for the preparation of 1-aminoanthraquinones which is useful for the preparation of chloro and other derivatives is treatment of a 1-chloroanthraquinone with *p*-toluenesulfonamide under the usual conditions of the Ullmann reaction and hydrolysis of the product with concentrated sulfuric acid. Thus 2-chloro-1-aminoanthraquinone (II) can be prepared[156] from 1,2-dichloroanthraquinone via the *p*-toluenesulfonamido compound (I); and aminobenzamidoanthraquinones (e.g., 1-amino-4-benzamidoanthraquinone) can be conveniently prepared from the corresponding chlorobenzamidoanthraquinones,[157] since only the arylsulfonyl group is eliminated from a 1-benzamido-4-, -5-, or -8-arylsulfonamidoanthraquinone treated with sulfuric acid at about 28°. β-Chlorine atoms in anthraquinone can also be replaced by amino groups in this manner under more severe conditions. (5) 1,4-Substituted aminoanthraquinones and aminohydroxyanthraquinones are prepared by amination of quinizarin. Unlike the Bucherer reaction, no sulfite, bisulfite, or condensing agent is necessary, and the amination proceeds in one step, merely by reaction under pressure and at an elevated temperature with aqueous ammonia ($AQ\text{-}OH + NH_3 \longrightarrow AQ\text{-}NH_2 + H_2O$). The method is specially valuable for the preparation of alkylamino- and arylaminoanthraquinones from the appropriate alkylamine or arylamine. Several of the simple aminoanthraquinones and their derivatives are used as cellulose acetate dyes.

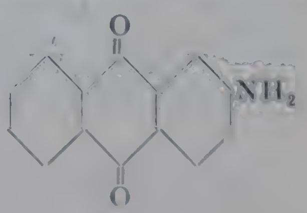


(I) (II)

α-Aminoanthraquinone (III; needles, m.p. 253°). Two methods have been mainly employed: reduction of the nitro compound and amination of the sulfonic acid. Since α-nitroanthraquinone is difficult to free from dinitro compounds, and the α-aminoanthraquinone is therefore admixed with diamines, this route has been abandoned in favor of the second method,



(III)



(IV)

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[156] ICI, BP 391,209.

[157] ICI, BP 375,848.

by which the pure amine is more readily obtained. Potassium anthraquinone-α-sulfonate, ammonia, and *m*-nitrobenzenesulfonic acid or arsenic pentoxide are heated at 180° in an autoclave for about 60 hours.[158]

β-**Aminoanthraquinone** (IV; red needles, m.p. 302°). The amination of anthraquinone-2-sulfonic acid proceeds in 92-94% yield by using sodium arsenate.[158] A second method, also employed in technical practice, proceeds through β-chloroanthraquinone (14 parts), which is heated with 25% ammonia (44), water (10), and 80% arsenic acid (0.64) in an autoclave at 200-215° for 24 hours.[7] β-Aminoanthraquinone of about 88% purity is obtained by filtration and washing; yield about 87%. Since β-chloroanthraquinone made by the phthalic anhydride route costs about the same as anthraquinone, the second process would appear cheaper, but the first has the advantage of using lower temperatures and pressures for the amination. Both the aminoanthraquinones are important intermediates for vat dyes. The α-compound is also valuable for the preparation of cellulose acetate dyes and acid dyes for wool and silk. Further, α-aminoanthraquinone (Fast Red Base AL) is employed to a limited extent in azoic dyeing.

2-Chloro-3-aminoanthraquinone (m.p. 310–311°), which is an important intermediate,[159] and 2,3-diaminoanthraquinone (red crystals, m.p. 353°) are best prepared by amination of 2,3-dichloroanthraquinone, obtained by condensation of phthalic anhydride with *o*-dichlorobenzene.[160]

1,2-Diaminoanthraquinone (violet needles, m.p. 303–304°). When α-aminoanthraquinone is sulfonated with potassium bisulfate at 210-240° with continuous removal of water vapor[161] or with 20% oleum (10 parts), 98% sulfuric acid (2) and anhydrous sodium sulfate (3) at 80–120° for a few hours,[162] 1-aminoanthraquinone-2-sulfonic acid can be obtained in about 95% yield; amination of this acid with 13 times its weight of 25% ammonia in presence of nitrobenzene, arsenic acid, and a little copper sulfate in an autoclave at 197° (45 atm. pressure) for 30 hours gives 1,2-diaminoanthraquinone.[7] It can also be prepared from 1,2-dichloro- or 1-chloro-2-amino- or 1-nitro-2-aminoanthraquinone. 1,3-Diaminoanthraquinone (red crystals, m.p. 290°), obtainable from 1,3-dibromoanthraquinone by the *p*-toluenesulfonamide route, is not used as a dye intermediate.

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[158] Iljinski and Nikolaeva, *Anilinokrasochnaya Prom.* **4**, 564 (1934); see also Bamberger and Allied Chemical and Dyestuff, USP 2,443,885. α-Aminoanthraquinone can be purified by refluxing with thionyl chloride in carbon tetrachloride; the 1-sulfinylamido derivative (AQ-N=S=O) separates on cooling. Steam-distillation to remove the solvent gives pure α-amino-anthraquinone by hydrolysis (Lecher, Eberhart and American Cyanamid, USP 2,479,943).

[7] See p. 50.

[159] See Chapter XXXIV, in which an alternative route is also mentioned; see also IG, BP 425,456; 425,854; ICI and Beckett, BP 427,251; 427,257.

[160] Groggins and Newton, *Ind. Eng. Chem.* **25**, 1030 (1933).

[161] Sandoz, BP 358,852.

[162] Seymour *et al.*, USP 2,413,790.

1,4-Diaminoanthraquinone (dark violet needles with metallic luster, m.p. 268°) is an important intermediate and is also used directly as a cellulose acetate dye. It can be made from 1,4- dichloroanthraquinone by the *p*-toluenesulfonamide method or from α-aminoanthraquinone by acylation of the amino group, nitration in the 4-position, hydrolysis, and reduction; but the technical method is to heat leucoquinizarin with ammonia and oxidize the intermediate product with manganese dioxide and sulfuric acid or nitrobenzene.[113] 1,5-Diaminoanthraquinone (deep red needles, m.p. 319°) is obtained by the reaction of anthraquinone-1,5-disodium sulfonate (15 parts), arsenic pentoxide (10) and 25% ammonia (53) at 175° (30 atm. pressure) in an autoclave (48 hours). The product is filtered, washed, and dried. *m*-Nitrobenzenesulfonate (11 parts) can be used in place of arsenic pentoxide, but the yield is lower.[163] Another method is the reaction of *p*-toluenesulfonamide with 1,5-dichloroanthraquinone.[164] 1,6-Diaminoanthraquinone (red needles, m.p. 292°) and 1,7-diaminoanthraquinone (red needles, m.p. 290°), prepared[165] from the reaction of 5-nitro- and 8-nitroanthraquinone-2-sulfonic acid with 25% ammonia and barium chloride at 230°, are of no interest as dye intermediates. This is also true of 1,8-diaminoanthraquinone (m.p. 262°), obtainable by reduction of the dinitro compound. 2,6-Diaminoanthraquinone (red-brown prisms, m.p 310–320°) is prepared by amination of anthraquinone-2,6-disulfonic acid at 200° and 45 atm. pressure. 2,7-Diaminoanthraquinone (orange-yellow needles, m.p. $>330°$), of no value as a dye intermediate, can be prepared similarly; it has also been obtained by reduction of 2,7-dinitroanthraquinone (Noelting, 1906), a product, together with anthraquinone, of the action of dilute nitric acid on anthracene.[166] It is doubtful whether these diaminoanthraquinones have as yet been obtained in absolute purity.

1,2,4-Triaminoanthraquinone (bluish red powder, m.p. $>300°$). α-Aminoanthraquinone can be nitrated to 2,4-dinitro-1-nitraminoanthraquinone, hydrolysis of which with sulfuric acid in phenol gives 2,4-dinitro-1-aminoanthraquinone (m.p. 270-272°); the 1,2,4-triamine is then obtained by reduction with aqueous ammonium sulfide.[167] Nitration of 1,4-, 1,5-, or 1,8- dibenzamidoanthraquinone results in the introduction of a nitro group in a vacant α-position; by reduction and subsequent hydrolysis of the benzoyl groups 1,4,5-triaminoanthraquinone is obtained.

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[113] See p. 78.

[163] *FIAT* **1016.**

[164] Scholl *et al.*, *Ber.* **62,** 107 (1929).

[165] Battegay and Claudin, *Bull. soc. chim. France* [4] **29,** 1027 (1921).

[166] Cf. Börnstein *et al.*, *Ber.* **59,** 2812 (1926).

[167] Terres, *Monatsh.* **41,** 603 (1921).

1,4,5,8-Tetraminoanthraquinone (red-brown needles, m.p. 332°), used as a blue dye for cellulose acetate, can be prepared[168] by amination of the corresponding tetrachloro compound, obtained by chlorination of anthraquinone under exposure to ultraviolet light; or by amination of the corresponding tetrahydroxy compound; or (in quantitative yield) by heating the 2-sulfonic acid (Alizarin Saphirol SE) or the 2,6-disulfonic acid (Alizarin Saphirol B) or 4,8-diamino-1,5-dihydroxyanthraquinone with ammonia and sodium bisulfite under pressure at about 120°; or by nitration and reduction of 1,5-dibenzamidoanthraquinone, followed by hydrolysis of the benzoyl groups.

The toxicity of aromatic amines. The hazards involved in the bulk production and use of some aromatic amines merit special consideration. In a recent review[169] on chemical carcinogenesis it is mentioned that the chemical agents, of which one can speak with some certainty as being responsible for bladder tumors, are encountered mainly in the manufacture of organic intermediates. Among the substances considered to be carcinogenic are aniline, toluidines, chlorotoluidines, benzidine, α- and β-naphthylamine, and several azo compounds such as 4-aminoazobenzene, 4-dimethylaminoazobenzene (Butter Yellow), and aminoazotoluenes. The highest incidence of cancer among workers in the dyestuff industry appears to be among those handling β-naphthylamine. The common feature of these carcinogenic compounds is that they are aromatic amines; the derived salts and the sulfonic acids are innocuous. The amines are therefore best converted into the hydrochlorides or sulfates if they are to be stored or sold for such purposes as diazotization and use in azoic dyeing. Although β-naphthylamine is a potent carcinogen, no case of cancer has been reported in workers exposed to phenyl-α- and β-naphthylamine. However, diphenylamine is suspect. The alkylanilines are apparently not carcinogenic, but they produce symptoms of methemoglobinemia. A large intake of milk and nonalcoholic fluids and a bath and complete change of clothes after the daily shift are among the prophylactic measures which minimize or eliminate the danger of carcinoma and bladder irritation in workers engaged in the manufacture of dye intermediates.

SECONDARY AND TERTIARY AMINES

There are several secondary and tertiary amines of the benzene and naphthalene series which are important intermediates for triphenylmethane and other classes of basic dyes. Aniline derivatives are prepared from the primary amine, while other methods similar to those employed for the primary amines themselves are available for the naphthylamine and aminoanthraquinone derivatives.

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[168] ICI, BP 364,141; 396,976; 391,859.

[169] *Brit. Med. Bulletin* 4, 309–426 (1947); see especially Goldblatt, "Occupational cancer of the bladder," *ibid.* p. 405.

When a primary amine (e.g., aniline) is alkylated by the usual methods employing the alkyl chlorides or sulfates, which can be prepared *in situ* by interaction of the appropriate alcohol and acid, the mono- or dialkylation cannot be carried to completion, and the product consists of a mixture of the secondary and tertiary amines, together with a small amount of the primary amine. Formation of mixtures is especially true of monoalkylation, in which some of the tertiary amine is invariably formed. However, suitable adjustment of conditions by which the secondary or tertiary amine is the major product and the efficiency of modern fractionation procedures have enabled the production of monomethyl-, monoethyl-, dimethyl-, and diethylanilines of adequate purity in excellent yields. In the laboratory a mixture of the three types of amines are readily separable by the Hinsberg reaction using benzene- or *p*-toluenesulfonyl chloride or by condensation with ethyl chlorocarbonate (chloroformate). On treatment with the arylsulfonyl

$$\mathrm{ArNH_2} + \mathrm{PhSO_2Cl} \longrightarrow \mathrm{ArNHSO_2Ph} \qquad \text{(I)}$$

$$\mathrm{ArNHR} + \mathrm{PhSO_2Cl} \longrightarrow \mathrm{ArNR{-}SO_2Ph} \qquad \text{(II)}$$

chloride the tertiary amine does not react and remains extractable with aqueous acid; the secondary amine forms a compound (II) insoluble in aqueous alkali, and the primary amine gives a compound (I) soluble in alkali. A method of separation, determination, and subsequent isolation of primary, secondary, and tertiary amines in a mixture of ring- and *N*-methylated aromatic amines by a modified Hinsberg reaction with pyridine-benzene as solvent has been described.[170] Another separation of secondary and tertiary amines involves treatment with phthalic or maleic anhydride; the secondary amine forms an aminic acid soluble in aqueous alkali.[171] Processes using chlorosulfonic acid have also been suggested.[172] Commercial monoalkylanilines as well as *m*-toluidine and *vic. m*-xylidine (*m*-2-xylidine) are purified readily through the complex salts of cuprous chloride and the hydrochlorides of the bases.[173] Primary, secondary and tertiary amines can all be characterized as the 2,4- or 3,5-dinitrobenzoates,[174] whereas tertiary amines can be characterized as their addition compounds with methyl *p*-toluenesulfonate.[175] Aniline, monomethylaniline, and dimethylaniline can be estimated in presence of one another colorimetrically by diazotization of aniline and coupling with Chicago acid and by the conversion of dimethylaniline into the intensely yellow *p*-nitroso compound.[176] Other similar mixtures can be estimated similarly.

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[170] Seaman *et al., JACS* **67,** 1571 (1945).

[171] du Pont, USP 1,991,787.

[172] Britton and Holmes, Dow Chem. Co., USP 1,890,246; 1,908,951.

[173] Jones and Kenner, *JCS* 711 (1932).

[174] Buehler, *et al., Ind. Eng. Chem. Anal. Ed.* **5,** 277 (1933); **6,** 351 (1934).

[175] Marvel *et al., JACS* **51,** 3638 (1929).

In the main technical preparation of the monoalkylanilines aniline hydrochloride is heated with the alcohol under pressure, but several other methods have been investigated. Examples in the case of monomethylaniline are (1) reduction of methyleneaniline with hydrogen (under catalysis) or with zinc dust and acetic acid and (2) the demethylation of dimethylaniline by heating with aniline hydrochloride. A maximum yield of 55% has been reported in both cases. The catalytic hydrogenation of the anil (Schiff's base) is generally applicable, and with the higher aldehydes much better yields (80–90%) can be obtained. In a modification a solution of the nitro compound and the aldehyde in alcohol is hydrogenated in presence of Raney nickel and sodium acetate at about 40 lbs. pressure when reduction to the primary amine, anil formation, and reduction to the secondary amine are achieved in one operation; yields of 31% to 96% are obtainable.[177]

$$\mathrm{PhN{=}CH_2} \xrightarrow{\mathrm{H_2}} \mathrm{PhNHMe} \qquad (1)$$

$$\mathrm{PhNMe_2 + PhNH_2} \longrightarrow \mathrm{2PhNHMe} \qquad (2)$$

$$\mathrm{PhNO_2 + RCHO} \xrightarrow{\mathrm{4H_2}} \mathrm{PhNHCH_2R + 3H_2O}$$

Secondary and tertiary amines can be prepared by reductive alkylation of nitrobenzene with aldehydes in presence of glacial acetic acid and Adams platinum oxide catalyst.[178] Aromatic amines can be alkylated by passing the mixed vapor of the amine and the appropriate alcohol over an alumina catalyst at 250–400°. This method[179] was used successfully during the war, and an experimental study of the reaction has been recently reported.[180] A solid dehydrating catalyst (e.g., precipitated aluminium oxide supported on bauxite) can be used for the vapor phase preparation of dimethylaniline at 200–230° from aniline and methanol.[181] Examples are quoted later of catalytic methods using ethers for alkylation.[182] Using alkylamines instead of ammonia, chlorobenzene can be converted into secondary amines.[181a]

A useful laboratory preparation of secondary amines is alkylation of an arylsulfonyl (usually the *p*-toluenesulfonyl) derivative (III) of the appropriate primary amine in alkaline solution and hydrolysis of the product (IV) with sulfuric acid. A suitable purification of secondary amines (Diepolder, 1899) consists in the reaction in hydrochloric acid

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[176] English, *Anal. Chem.* **19**, 457 (1947).

[177] Emerson and Mohrman, *JACS* **62**, 69 (1940); Major, *ibid.* **53**, 1901, 2803, 4373 (1931); USP 1,978,433; Emerson, Organic Reactions, IV, Wiley, New York, 1948, p. 174.

[178] Emerson, USP 2,414,031.

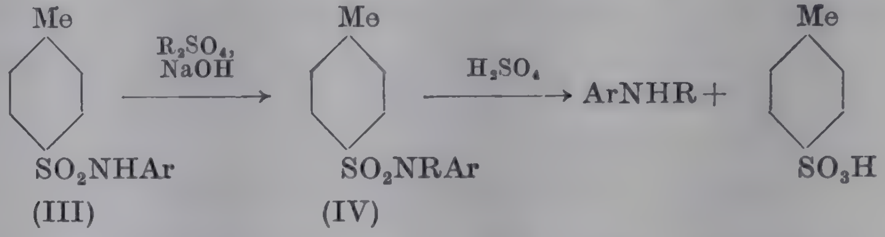
[179] Röhm and Haas Co., FP 734,404.

[180] Earl and Hills, *JCS* 973 (1947).

[181] Maxted, BP 577,901. See also Hughes *et al.*, *Ind. Eng. Chem.* **42**, 787 (1950).

[181a] Hughes, USP 2,455,931-2.

[182] See also Markert, BP 275,377; Roy, *J. Indian Chem. Soc.* **5**, 383 (1928).



solution with sodium nitrite, when an *N*-nitroso compound is formed, which is isolated and denitrosated by reduction with stannous chloride and hydrochloric acid.

$$\text{ArNHR} \longrightarrow \text{ArN(NO)R} \xrightarrow{6\text{H}} \text{ArNHR} + \text{NH}_3 + \text{H}_2\text{O}$$

Thus, *N*-ethyl-*m*-toluidine, prepared from *m*-toluidine and ethyl bromide at room temperature, can be purified by this procedure.[183] Reduction of the *N*-nitroso derivatives of monoalkylanilines with zinc dust and acetic acid yields the α-substituted phenylhydrazines; thus *N*-nitroso-*N*-methylaniline (methylphenylnitrosamine)[184] gives α-methyl-α-phenylhydrazine ($PhNMe\text{-}NH_2$),[185] which like phenylhydrazine is a useful reagent for characterization of sugars.

Monomethylaniline (colorless oil, b.p. 194°) is manufactured by treatment of aniline with methanol and hydrochloric acid at about 190° in an autoclave under conditions leading to the formation of as little dimethylaniline as possible. While the latter has a boiling point almost identical with that of monomethylaniline, aniline (b.p. 184°) and monomethylaniline differ sufficiently in b.p. to be separable by fractional distillation.

Dimethylaniline (colorless oil, m.p. 2.5°, b.p. 192°) is among the most largely used intermediates. It is manufactured in about 95% yield by heating aniline (100 parts), methanol (110), and sulfuric acid (10) for 6 hours at about 200°.[185a] While the active methylating agent, dimethyl sulfate, is thus formed, dimethyl ether is formed as a by-product with consequent development of high pressures. Strong cast-steel autoclaves are therefore employed. Pure anhydrous aniline and methanol free from acetone must be used. At the end of the reaction the pressure is released, and the vapors drawn off through a condenser for the recovery of excess methanol. The product is then made alkaline and steam distilled. The oil is separated and purified by fractional distillation. Dimethylaniline can be prepared in 99.5–99.7% yield from aniline and methanol (1 : 2.5 moles) with phosphorus trichloride (0.9% of the mixture) heated at 270–280° at 70–110 atm. pressure for 7 hours when monomethylation is complete; after cooling to 180° and distillation of methanol and water, more phosphorus trichloride and methanol are added, and the mixture is heated again for 3 hours at 250–260° and 70–90 atm. pressure. In an interesting method[6] used for manufacture of dimethyl-*o*-toluidine (V; b.p. 184.8°) a mixture of *o*-toluidine and dimethyl ether is passed over an alumina catalyst; the yield is about 90%.

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[183] Buck and Ferry, *OSCV* II, p. 290.

[184] Hepp (1877); Hartman and Roll, *ibid.* p. 460.

[185] Fischer (1878); Hartman and Roll, *ibid.* p. 418.

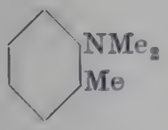
[185a] See also Shreve *et al.*, *Ind. Eng. Chem.* **42**, 791 (1950).

Monoethylaniline (colorless oil, b.p. 204°), which unlike the methylanilines is a more important intermediate than diethylaniline and is also more easily prepared, is manufactured by the reaction, under pressure and at about 180°, of aniline hydrochloride with a slight excess of ethanol, or by the reaction of aniline and ethanol catalyzed by phosphorus trichloride.

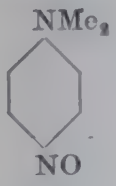
Diethylaniline (b.p. 215.5°). While sulfuric acid is used in the preparation of dimethylaniline, diethylaniline is prepared from aniline hydrochloride and ethanol, since sulfuric acid promotes nuclear alkylation; alternatively aniline, ethanol, aqueous hydrochloric acid, and phosphorus trichloride as catalyst can be heated at 280° and 100 atm. pressure.

The presence of aniline in dimethylaniline is detected by the addition to an ether solution of a few drops of concentrated sulfuric acid when aniline sulfate is precipitated. Monomethylaniline can be detected, as well as estimated, by the rise in temperature after addition of acetic anhydride under standard conditions. A rapid colorimetric method for the estimation of dimethylaniline in admixture with aniline and monomethylaniline is based on acetylation of the latter compounds, followed by nitrosation.[186]

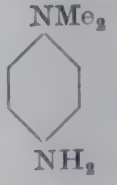
Dimethylaniline and diethylaniline are nitrosated very readily and quantitatively in aqueous hydrochloric acid solution by sodium nitrite at 0-5°. *p*-Nitrosodimethylaniline (VI; large green plates, m.p. 92°) is an intermediate for Methylene Blue and other basic dyes; it is also a valuable accelerator in vulcanization of rubber. Reduction of the hydrochloride of (VI) by iron and 1% hydrochloric acid at about 40° gives *p*-aminodimethyl-



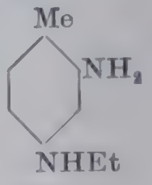
(V)



(VI)



(VII)



(VIII)

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[6] See p. 50.

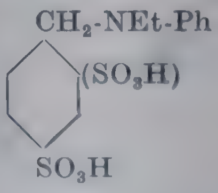
[186] Haslam and Hearn, *Analyst* **69,** 141 (1944); see also Blumrich and Bandel, *Angew. Chem.* **54,** 374 (1941).

aniline (VII; colorless needles, m.p. 41°), an intermediate for azo dyes, basic dyes such as Methylene Blue, and sulfur dyes. *p*-Aminodiethylaniline (b.p. 260-2°) is similarly prepared. By nitration of dimethylaniline in presence of a large excess of sulfuric acid, the *m*-nitro compound (m.p. 60–61°; b.p. 280-5°) is obtained as the major product (about 80%), together with the *p*-isomer (m.p. 163°); when the reaction mixture is poured into water the latter is precipitated, and the *m*-compound can be isolated on neutralization of the filtrate. Acid reduction gives *m*-aminodimethylaniline (b.p. 268–270°/740 mm.). Mixed acid nitration of *N*-monoethyl-*p*-toluidine, followed by reduction, furnishes 4-ethylamino-*o*-toluidine (VIII).

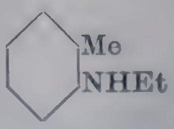
The methyl- and ethylanilines were the only alkylanilines used as dyestuff intermediates for many years, but the higher homologs up to dodecyl-, cetyl-, and octadecylanilines are now being used because of their ability to modify the shade and improve wet fastness. In the case of tertiary amines, one of the alkyl groups is usually methyl or ethyl. These secondary and tertiary amines can be prepared by heating aniline or monomethyl- or monoethylaniline with the desired alkyl halide. Another procedure is the replacement of one of the methyl groups (e.g., by a dodecyl group) in dimethylaniline.[187] *n*-Butylaniline (b.p. 240°/756 mm.) is obtained in about 58% yield, the balance of the aniline being mostly recoverable, by heating aniline with an equal weight of butanol and 12% of phosphorus trichloride at 270° for 3 hours in an autoclave.

***N*-Benzylaniline** (colorless needles or prisms, m.p. 38°, b.p. 310°) is prepared by the reaction of aniline with benzyl chloride in presence of aqueous sodium bicarbonate at 90–95° for a few hours.[188] Benzylmethylaniline (b.p. 305–306°) and benzylethylaniline (b.p. 285–286°/710 mm.) are important intermediates for violet and green acid triphenylmethane dyes, the benzyl group functioning as a carrier for sulfonic groups. They are prepared by heating the monoalkylaniline with benzyl chloride, and by sulfonation the mono- and disulfonic acids (e.g., IX) can be prepared.

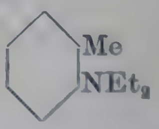
***N*-Ethyl-*o*-toluidine** (X; b.p. 214–214.5°) and *N*,*N*-diethyl-*o*-toluidine (XI; b.p. 209–210°) are manufactured[10, 189] by passing a mixture of



(IX)



(X)



(XI)

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[187] Willischmidt, Albrecht, and IG, DRP 611,283.

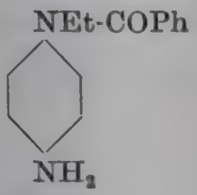
[188] Willson and Wheeler, *OSCV* I, p. 102.

[10] See p. 50.

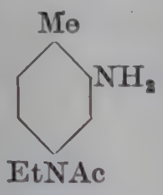
[189] IG, BP 421,596.

o-toluidine and diethyl ether vapors over an alumina catalyst at 250–255°. The product is a mixture of about 60% of (X), 30% of (XI), and 10% of unconverted *o*-toluidine, which are separated by fractional distillation.

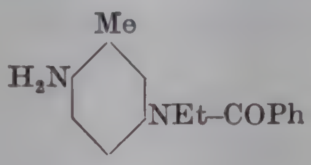
***N*-Benzoyl-*N*-ethyl-*p*-phenylenediamine** (XII) is obtained by nitration and reduction of *N*-benzoylmonoethylaniline. *N*-Ethyl-*p*-toluidine (b.p. 217°) is used for making 2-amino-*N*-ethylacet-*p*-toluidide (XIII) by acetylation, nitration, and reduction. Benzoylation of monoethyl-*m*-toluidine, followed by nitration and reduction, gives 6-amino-*N*-ethylbenz-*m*-toluidide (XIV).



(XII)



(XIII)



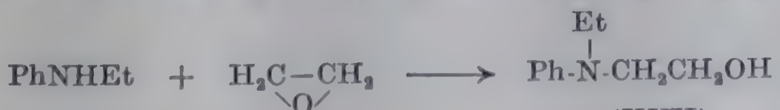
(XIV)

As intermediates for azo dyes for wool with high wet fastness, aromatic amines having heavy alkyl groups in the nucleus are being employed; they are also useful for the production of textile auxiliary agents. Lower homologs, such as *p*-*sec*- and *p*-*tert*-butylaniline, are obtained by the action of the appropriate alcohol on acetanilide or on acet-*o*-toluidide in a solvent in presence of aluminium chloride, followed by hydrolysis of the acetyl group.[190] The higher homologs can be prepared by heating the amine (aniline, *o*-toluidine, etc.) and its hydrochloride with an alcohol such as dodecyl alcohol and zinc chloride or cobalt chloride;[191] *p*-dodecylaniline of high purity is thus obtained.

A series of ethanolamine derivatives are used in the preparation of azo dyes for cellulose acetate. From the reaction of aniline with a fifth of its weight of ethylene oxide at 60–65° in an autoclave for a few hours and fractionation of the product, *N*-β-hydroxyethylaniline (XV) is obtained in 85% yield, based on the aniline recovered. If 0.95 part of ethylene oxide for one of aniline and a temperature of 95–110° are used, the product (88% yield) is *N*,*N*-bis-β-hydroxyethylaniline (XVI). Further examples

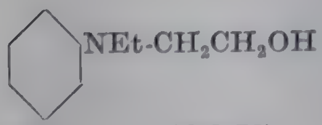
$PhNHCH_2CH_2OH$ (XV)

$PhN(CH_2CH_2OH)_2$ (XVI)

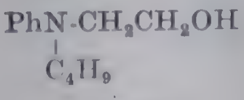


$$PhNHEt + H_2C{-}CH_2(O) \longrightarrow Ph\text{-}\underset{}{\overset{Et}{N}}\text{-}CH_2CH_2OH$$

(XVII)



(XVIII)



$$Ph\underset{C_4H_9}{N}\text{-}CH_2CH_2OH$$

(XIX)

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[190] U. S. Industrial Alcohol Co., BP 465,650.

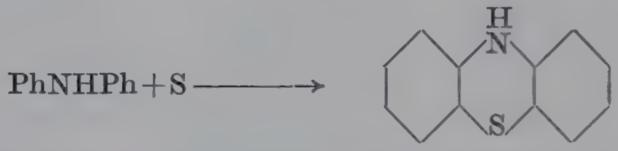
[191] Coffey, Haddock and ICI, BP 468,226.

are (XVII) and the analogous compounds (XVIII; XIX) from *N*-ethyl-*m*-toluidine and *n*-butylaniline respectively. They are obtainable in nearly quantitative yield by heating the appropriate monoalkylaniline with ethylene oxide at about 150° in an autoclave for a few hours.[10]

Diphenylamine (colorless plates, m.p. 54°, b.p. 302°) is obtained by heating aniline and its hydrochloride under pressure at about 230°. After removal of unreacted aniline with dilute hydrochloric acid, the residual diphenylamine is purified by vacuum distillation. In addition to its being a

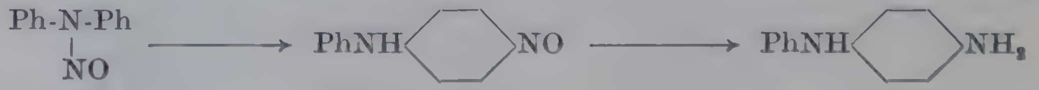
$$PhNH_2 + PhNH_3Cl \longrightarrow PhNHPh + NH_4Cl$$

dye intermediate (mainly for the preparation of Metanil Yellow) a notable use for diphenylamine is for conversion, by reaction with sulfur, into the



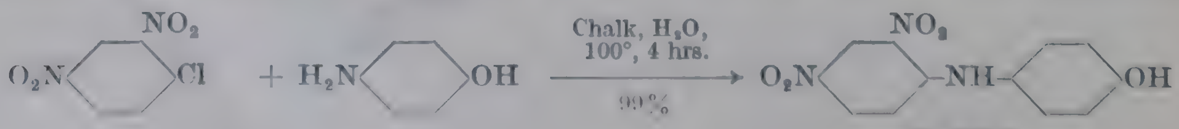
(XX)

largely used insecticide and veterinary anthelmintic, thiodiphenylamine or phenothiazine (XX; yellow plates, m.p. 182°). Sulfonation of diphenylamine with concentrated sulfuric acid and sodium sulfate at 130° gives a disulfonic acid, from which the 4-monosulfonic acid is obtained by dilution with water and heating at 125° until the removal of one sulfonic group is complete.[6] The deep blue color produced by addition of sodium nitrite solution to a solution of diphenylamine in concentrated sulfuric acid is a sensitive test for nitrous acid. *N*-Methyldiphenylamine (b.p. 296°) is prepared by heating diphenylamine with methanol and hydrochloric acid under pressure. *p*-Aminodiphenylamine (XXIII; Diphenyl Black Base), used in dyeing Aniline Blacks, is prepared[6] by treatment of diphenylamine in chloroform solution with sodium nitrite and sulfuric acid, isomerization



(XXI) (XXII) (XXIII)

of the *N*-nitroso compound (XXI) to the hydrochloride of the 4-nitroso compound (XXII) by hydrogen chloride, liberation of the free base with alkali, and reduction with sodium polysulfide. Derivatives of diphenylamine (e.g., XXIV), prepared by condensation of reactive chlorobenzene



(XXIV)

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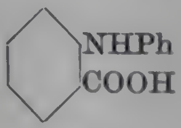
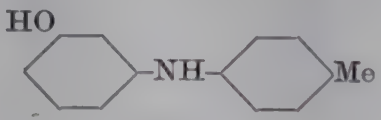
[10] See p. 50.

[6] See p. 50.

derivatives such as 1-chloro-2,4-dinitrobenzene with *p*-aminophenol, *p*-phenylenediamine, or 5-aminosalicylic acid, are intermediates for sulfur dyes.[192] *o*-Nitrodiphenylamines are of interest as reagents for synthesis on account of their convertibility into phenazines, benzocinnolines, carbazoles, oxazines, and benzimidazoles.[193] Another route to diphenylamine derivatives is the reduction of indophenols.[141] Diphenylamine-2-carboxylic acid (needles; m.p. 184°) (XXV) is prepared by treatment of aniline with *o*-chlorobenzoic acid and caustic potash or potassium carbonate in presence of copper at about 125° for a few hours. *m*-Hydroxydiphenylamine and *m*-hydroxyphenyl-*p*-tolylamine (XXVI) are obtained by the reaction of resorcinol with aniline and *p*-toluidine, respectively, at 190–230° in presence of sulfanilic acid during several hours, and continuous distillation of the water formed.[6]

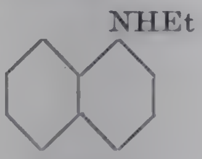


(XXV)

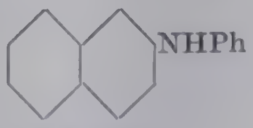


(XXVI)

N-Ethyl-α-naphthylamine (XXVII; b.p. 191°/16 mm.) and *N*-phenyl-α-naphthylamine (m.p. 62°) are intermediates for the Victoria Blues. The former is prepared by heating α-naphthylamine with ethyl chloride, chalk, and water at 170° and 10 atm. pressure; on cooling, the crystalline hydrochloride of ethyl-α-naphthylamine separates; the base is liberated by means of soda ash and purified by vacuum distillation. *N*-Phenyl-α-naphthylamine, used as an antioxidant in the rubber industry, is prepared by heating α-naphthylamine or α-naphthol with aniline in presence of a catalyst (e.g., *p*-toluenesulfonic acid,[6] sulfanilic acid, or ammonium iodide)[194] in an autoclave at 220–230° for 24 hours. The product is purified by vacuum distillation.



(XXVII)



(XXVIII)

N-Methyl- and *N*-ethyl-β-naphthylamine (b.p. 317°/766 mm. and 316–317°, respectively) can be prepared by heating β-naphthol with the alkylamine under pressure at about 220° or by heating β-napthylamine with the alkyl bromide or the alkyl *p*-toluenesulfonate in presence of alkali.[195] The aryl-β-naphthylamines are prepared by heating β-naphthol with the arylamine or its hydrochloride under pressure at about 200°. Thus *N*-phenyl-β-naphthylamine (XXVIII; m.p. 108°), an important antioxidant in the rubber industry, is obtained in nearly quantitative yield from the reaction of β-naphthol with aniline (1.2 parts) and iodine (0.01 part) at 190° for 7 hours. The IG employ a process[6, 194] in which β-naphthol, aniline, and sulfuric acid (about 1% of the weight of β-naphthol) are heated under conditions in which water continuously distils and aniline returns to the still. Azo dyes from the *N*-aryl-β-naphthylamines are useful for acetate silk.

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[192] See Chapter XXXV.
[193] See for instance Slack and Slack, *Nature* **160**, 437 (1947).
[141] See p. 88.
[6] See p. 50.
[194] Hodgson and Marsden, *JCS* 1181 (1938).

ALKYLAMINO- AND ARYLAMINOANTHRAQUINONES

The α-alkylaminoanthraquinones are important as dyes for acetate silk, and the arylaminoanthraquinones as intermediates for acid and vat dyes. *N*-Alkylation and -arylation methods similar to those employed in the benzene and naphthalene series are applicable, but the preferred procedures are the replacement of a sulfo, halogen, nitro, hydroxy, or alkoxy substituent by the alkylamino or arylamino group. 1-Methylaminoanthraquinone (yellowish red needles, m.p. 170°) is obtained by heating potassium anthraquinone-1-sulfonate with about 10 times its weight of 25% aqueous methylamine, sodium *m*-nitrobenzenesulfonate (0.17 part), and copper sulfate (0.25 part) at about 130° in an autoclave for several hours.[11, 196] Halogen in the α-position is more labile than that in the β-; thus 2-bromo-1-amino-4-*p*-toluidinoanthraquinone is obtained in excellent yield by heating 2,4-dibromo-1-aminoanthraquinone with *p*-toluidine in presence of a copper salt and an acid-binding agent such as potassium carbonate; *p*-toluidine itself or amyl alcohol or nitrobenzene can be used as solvent. The replacement of a hydroxyl group is a practicable process when the leucoanthraquinone is used and boric acid is added so that a boric ester, which condenses readily with amines, is formed. Quinizarin and its derivatives are especially amenable to this reaction, and one or more hydroxyl groups can be progressively replaced.[113] 1,4-Bis-methylaminoanthraquinone (II), a valuable blue dye for cellulose acetate, is prepared by heating leucoquinizarin with methylamine under pressure; the product, probably constituted as (I) and not the anthrahydroquinone derivative, is readily oxidized by air or by hydrogen peroxide to (II). When (II) is heated with sulfuric acid, partial demethylation takes place, and 1-amino-4-methylaminoanthraquinone (III; m.p. 195°), a bluish violet dye for cellulose acetate, is obtained. Another method for the preparation of (III) is to heat 1-amino-4-methoxyanthraquinone with methylamine under controlled conditions.[197]

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[195] Morgan and Evan, *JCS* **115,** 1141 (1919); Slotta and Franke, *Ber.* **63,** 678 (1930).

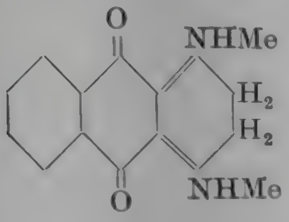
[6] See p. 50.

[194] See p. 103.

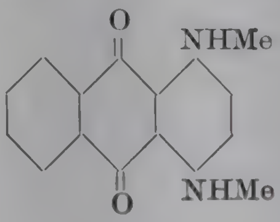
[11] See p. 50.

[196] See also Wilson, Dickey and Allen, *Org. Syntheses* **29,** 66 (1949). N-Methylation in the anthraquinone series can be effected by heating the primary amine with formaldehyde and oxalic acid; Erkkila, Hoare and Allied Chemical and Dyestuff, USP 2,443,899.

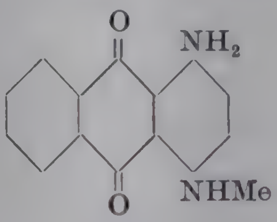
[113] See p. 79.



(I)



(II)

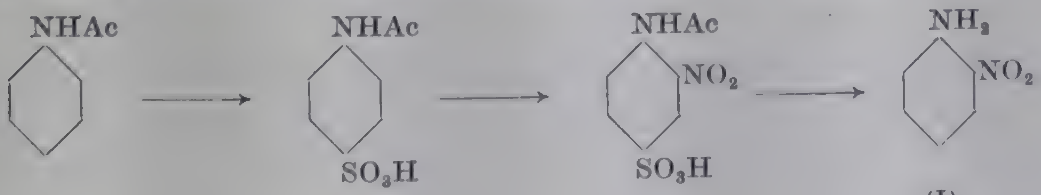


(III)

N-β-Hydroxyethyl derivatives are especially important as acetate silk dyes and they are prepared by condensation of the appropriate aminoanthraquinone with ethylene chlorohydrin or with ethylene oxide.

NITROANILINES

The nitroanilines are very important intermediates. When acetanilide is nitrated in concentrated sulfuric acid by mixed acid below 20°, a mixture of about 75% of the *p*-nitro compound and 20% of the *o*- is obtained. Alternatively, acetanilide is dissolved in 78% nitric acid, cooled to 0-5°, and added to excess of 97.6% sulfuric acid cooled to −1°; the temperature is lowered to −10° when 20% of the acetanilide has been added.[198] At the end of the reaction the mixture is blown into hot water, and the precipitated *p*-nitroacetanilide is filtered. The *o*-compound can be recovered from the filtrate by salting out. Warming with caustic soda solution then leads to the respective nitroanilines. The nitration of benzylideneaniline gives a nearly theoretical yield of the *p*-nitro compound. *o*-Nitroaniline (I) can be prepared by sulfonation of acetanilide with oleum to form the *p*-sulfonic acid, nitration, and desulfonation with dilute sulfuric acid of b.p. 120°.[199] In the main technical method[6] for the preparation of *o*- and *p*-nitroaniline the corresponding chloronitrobenzene is heated with about 5 times its weight



(I)

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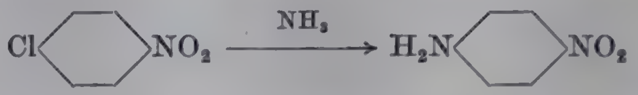
[197] Ciba, BP 296,662.

[198] Bast and American Cyanamid, USP 2,406,578.

[199] See also Ehrenfeld and Puterbaugh, *OSCV* I, p. 388.

[6] See p. 50.

of 27% ammonia at 175–200° (40-45 atm. pressure) in an autoclave for about 8 hours. Careful control of temperature and pressure are necessary, since the reaction is exothermic, and an explosion can occur if the pressure



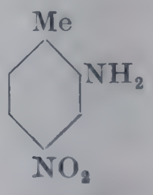
(II)

is not released by blowing off ammonia to an absorber when the temperature and pressure tend to exceed 200° and 45 atm. The nitroaniline separates on cooling (nearly quantitative yield), and can be purified by crystallization from water, the procedure for *p*-nitroaniline being to heat with water under pressure at 130°. In view of the occurrence of occasional explosions, the IG regarded the amination of chloronitrobenzenes in large batches as a major hazard, and developed a continuous process in which the chloronitrobenzene and 40% ammonia were forced through stainless steel coils at 200 atm. pressure and 230–250°, the conversion being 96–99%. The method could be utilized also for the more reactive dichloronitrobenzenes (2,5- and 3,4-) to produce 4-chloro-2-nitroaniline and 2-chloro-4-nitroaniline by use of more dilute ammonia (25–27%).[200]

***p*-Nitroaniline** (II; yellow needles, m.p. 148°) is used for the preparation of azo dyes and pigments, and in large quantities for dyeing Para Red; for azoic dyeing it is marketed as Fast Red GG Base and as the stabilized diazonium salt, Nitrazol C (IG). Chlorination of *p*-nitroaniline in aqueous hydrochloric acid by sodium chlorate at 20–25° yields 2,6-dichloro-*p*-nitroaniline (yellow needles, m.p. 195°).

***o*-Nitroaniline** (golden yellow needles or plates, m.p. 71.5°) is used in azoic dyeing as Fast Orange GR Base.

***m*-Nitroaniline** (yellow needles, m.p. 114°; Fast Orange R Base) is prepared by reduction of *m*-dinitrobenzene with sodium sulfide or sodium hydrogen sulfide in presence of a little magnesium sulfate. The very important 4-nitro-*o*-toluidine (III; m.p. 107°; Fast Scarlet G Base) is



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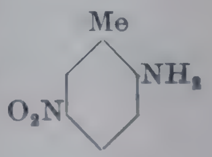

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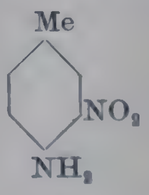

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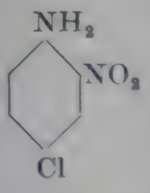

(VI)

prepared from *o*-toluidine by nitration, which has to be carried out at −10° by the addition of 98% nitric acid (2 parts) to a solution of *o*-toluidine (3 parts) in 98% sulfuric acid (15 parts). On running the nitration mixture into water, keeping the temperature at 65°, and then cooling to 25°, the sulfate of (III) separates, and the more soluble sulfate of 6-nitro-*o*-toluidine remains in solution. The separation however is not complete, and commercial Fast Scarlet G Base contains 4–5% of the 6-nitro isomer.[8] 5-Nitro-*o*-toluidine (IV; yellow needles, m.p. 129°; Fast Red RL Base) is obtained[6] in an overall yield of about 80% by nitration of *N*-benzenesulfonyl-*o*-toluidine with 62% nitric acid in chlorobenzene solution at 40–50°, and hydrolysis of the benzenesulfonyl group in the resulting product with 95% sulfuric acid (60°, 1 hr.).[201] On nitration of acet-*p*-toluidide and hydrolysis of the acetyl group, the product is 3-nitro-*p*-toluidine (V; red leaflets, m.p. 117°; Fast Red GL Base). 2-Chloro-5-nitro- and 4-chloro-3-nitroanilines (orange needles, m.p. 95–96°; and yellow needles, m.p. 103°, respectively) are formed in about equal amounts by the monoreduction of 1-chloro-2,4-dinitrobenzene by stannous chloride in glacial acetic acid.[202] When 2,5-dichloronitrobenzene is heated with 27% ammonia at about 165° under pressure, a 99% yield[6] of 4-chloro-2-nitroaniline (VI; m.p. 116–117°; Fast Red 3GL Base) is obtained.

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[200] *BIOS* 1147.

2,4-Dinitroacetanilide (m.p. 121°) can be prepared by dinitration of acetanilide or by acetylation of dinitroaniline with acetic anhydride at about 115° in presence of a little monohydrate; on reduction with iron and aqueous sulfuric acid at 90–95°, it gives 2,4-diaminoacetanilide (m.p. 158–159°), an intermediate for brown sulfur dyes. 2,4-Dinitroaniline (yellow needles, m.p. 180°) is obtainable by hydrolysis of dinitroacetanilide or by amination of 2,4-dinitrochlorobenzene either with aqueous ammonia at about 100° under pressure or by reaction with ammonium acetate at 170° in a current of ammonia.[203, 204] 2,4-Dinitro-*N*-methylaniline is prepared by the addition of aqueous methylamine and caustic soda to chlorodinitrobenzene in boiling water. 4-Nitro-*m*-phenylenediamine (VII; yellowish red prisms with a blue reflex, m.p. 161°) is a fur dye and an intermediate for azo dyes. Two methods of preparation are available: reaction of 4-nitroaniline-3-sulfonic acid with ammonia under pressure at 180° or nitration of diformyl *m*-phenylenediamine, followed by hydrolysis of the formyl groups.[205]

Nitronaphthylamines.[206] By nitration of α-naphthylamine below −1° the 5- and 8-nitro compounds (red needles, m.p. 118.8° and 96–97°) are obtained, separable by the sparing solubility of the former in aqueous sulfuric acid.[207, 208] Nitration of acet-α-naphthalide gives a mixture of the 2- and 4-nitro compounds (m.p. of the amines 144° and 195°), which can be separated by deacetylation and precipitation of 4-nitro-1-naphthylamine as the hydrochloride from a nitrobenzene solution.[209] 3-Nitro-1-naphthylamine (m.p. 136–137°) is prepared by the reduction of 1,3-dinitronaphthalene with ammonium or sodium sulfide in alcohol.[210] 5- and 8-Nitro-2-naphthylamines (m.p. 143.5° and 104–105°) are obtained by nitration of β-naphthylamine, and the 1- (60%), 6-, and 8-nitro compounds by nitration of acet-β-naphthalide.[211] The nitro-2-naphthylamines, other than the 1-compound, can be coupled with diazonium salts to form the 1-azo dyes, and these on oxidation to the triazole, followed by reduction of the nitro group, give aminonaphthotriazoles such as (VIII), used as azo dye intermediates.[212]

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[8] See p. 50.

[6] See p. 50.

[201] For a study of the nitration of the acet-toluidides, and the absorption spectra of the ten mononitrotoluidines, see McGookin *et al.*, *J. Soc. Chem. Ind.* **58,** 152 (1939); **60,** 297 (1941); *JCS* 901 (**1934**).

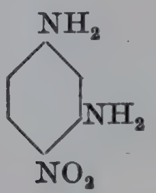
[202] Hodgson and Dodgson, *ibid.* 870 (**1948**).

[203] Wells and Allen, *OSCV* II, p. 221.

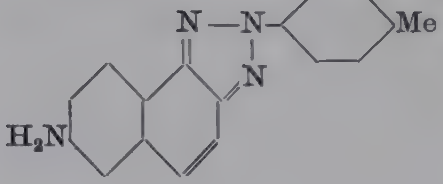
[204] For the preparation of other dinitroanilines, see Welsh, *JACS* **63,** 3276 (1941).

[205] AGFA, DRP 130,438; Gordonov, *Anilinokrasochnaya Prom.* **4,** 277 (1934).

[206] Hodgson and Hathaway, *J. Soc. Dyers Colourists* **63,** 231 (1947), have reviewed the methods of preparation of the various nitronaphthylamines.



(VII)



(VIII)

HYDROXYLATION

The main general method is the alkali fusion of sulfonic acids ($Ar\text{-}SO_3Na + 2NaOH \longrightarrow Ar\text{-}ONa + Na_2SO_3 + H_2O$). One or more sulfonic groups can be progressively replaced in polysulfonic acids. The alkali generally employed is caustic soda, but the addition of caustic potash is sometimes an advantage. Patents[213] also refer to the use of alkali carbonates at 350–380° in an atmosphere of steam and of steam alone acting on the sodium sulfonate at about 450°. A second general reaction is hydrolysis of chloro compounds ($Ar\text{-}Cl + 2NaOH \longrightarrow Ar\text{-}ONa + NaCl$), and as in the parallel amination process, the conditions under which replacement can be effected depend on the other substituents. In the Raschig process for the manufacture of phenol, chlorobenzene is hydrolyzed by steam in presence of a silica catalyst ($PhCl + H_2O \longrightarrow PhOH + HCl$). Benzene can be oxidized to phenol in yields of 0.3 to 1.9% by passing a

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[207] Morgan and Jones, *J. Soc. Chem. Ind.* **42**, 341T (1923).

[208] The 5- and 8-nitro-1-naphthylamines can also be prepared by partial reduction of the dinitronaphthalenes; Ruggli and Knapp, *Helv. Chim. Acta* **13**, 763 (1930); ICI and Hodgson, BP 392,414.

[209] Hodgson and Walker, *JCS* 1205 (**1933**).

[210] Hodgson and Birtwell, *ibid.* 75 (**1944**).

[211] Vesely and Jakes, *Bull. soc. chim.* **33**, 942 (1923); Bell, *JCS* 2784 (**1929**); Hartman and Smith, *OSCV* II, p. 438.

[212] Morgan *et al.*, BP 191,797; *J. Soc. Chem. Ind.* **41**, 1T, 61T (1922).

[213] Illyukevich, RP 65,855; 66,491.

mixture of benzene and air through a reaction zone at 400–800° free from catalytic material with control of velocity and pressure;[214] the reaction can be carried out in vessels coated with boric oxide;[215] or in presence of a vanadium pentoxide catalyst.[215a] Amines can be converted into phenols by a variety of methods. Replacement through the diazonium reaction ($ArNH_2+HNO_2+HCl \longrightarrow ArN_2Cl \xrightarrow{H_2O} ArOH+N_2+HCl$) is a useful laboratory method, which finds technical application in a few cases, such as *m*- and *p*-cresol. In the naphthalene series hydrolysis of an amino group can be effected directly by heating with acid or alkali under pressure ($ArNH_2+H_2O \longrightarrow ArOH+NH_3$);[216] thus α-naphthol can be prepared from α-naphthylamine, and Nevile and Winther's acid (1-naphthol-4-sulfonic acid) from naphthionic acid. The Bucherer reaction, mentioned earlier among amination methods, is valuable in its reverse form for the preparation of naphthols by heating the amine with excess of sodium bisulfite solution and hydrolyzing the intermediate sulfite ester with alkali ($ArNH_2 \xrightarrow{NaHSO_3} NH_3+Ar\text{-}O\text{-}SO_2Na \xrightarrow{2NaOH} ArONa+Na_2SO_3+H_2O$). An amino group adjacent or *para* to a nitro group is readily replaced by hydroxyl with boiling caustic soda solution; thus 1-nitro-2-naphthylamine gives a nearly quantitative yield of 1-nitro-2-naphthol.[217] Nitroamines (e.g., *p*-nitroaniline), diamines, and aminophenols, and especially *p*-nitrosodialkylanilines, can be hydrolyzed to the corresponding phenols in the benzene series, but there are better methods available. In the Bohn-Schmidt reaction, applicable only to hydroxyanthraquinones, hydroxyl groups are introduced by means of fuming sulfuric acid; alizarin can be hydroxylated in this manner to 1,2,5,8-tetrahydroxyanthraquinone (Alizarin Bordeaux B).[56]

The alkali fusion of sulfonic acids is carried out at a temperature of about 300° in a cast-iron pot provided with a powerful scraper agitator. Solid caustic soda and a little water are melted together, and the sodium arylsulfonate is added. The quantity of water, temperature and time of fusion depend on the sulfonic acid; these conditions are particularly important in the case of naphthalenepolysulfonic acids, since they govern both the number and position of the sulfonic groups replaced. It is sometimes preferable to use a considerable amount of water with the alkali and to carry out the hydrolysis under pressure in an autoclave. The reaction mixture is then diluted, and the phenol liberated by acidification, after filtration of precipitated sodium sulfite if possible. The sulfur dioxide evolved is compressed and used. The phenol is then isolated by filtration, steam distillation, or solvent extraction. Naphtholsulfonic acids are worked up like the naphthalenesulfonic acids.

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[214] Solvay Process Co., USP 2,223,383; see also Krieble and Denton, USP 2,439,812; 2,440,233; Denton *et al.*, *Ind. Eng. Chem.* **42,** 777 (1950).

[215] Solvay Process Co., USP 2,328,920; see also USP 2,415,101.

[215a] Schlesman, Denton, and Bishop, USP 2,456,597. See also Bremner and ICI, BP 628,503.

[216] See also Cross and ICI, USP 2,438,694.

[217] Andreoni and Biedermann (1873); Hartman, Byers, and Dickey, *OSCV* II, p. 451.

[56] See p. 62.

Phenol.[218] The optimum conditions[219] for the conversion of sodium benzenesulfonate into phenol are: about 3 moles of caustic soda for one of sodium benzenesulfonate added gradually in the course of a few hours, temperature of fusion 300°, and efficient stirring to avoid local overheating. Exclusion of air from the melt is an advantage. A yield of 90% or more can be obtained. Among the by-products formed under unfavorable conditions are dihydroxydiphenyls, diphenyl ether, thiophenol, and carbon dioxide.[219] Crude phenol is purified by vacuum distillation. In the IG process at Leverkusen 3.5 moles of caustic soda (as a 78% aqueous solution) per mole of sodium benzenesulfonate and a fusion temperature of 320–340° were employed; a yield of 89–91% of phenol, m.p. 40.6°, was obtained on the basis of the benzene used for sulfonation. No hydroxydiphenyls were formed, but there was a breakdown to sodium acetate corresponding to about 5% of the theoretically possible phenol.[146]

Sulfonation of benzene in presence of high-boiling naphtha cuts and fusion of sodium benzenesulfonate with 50% aqueous caustic soda under kerosene are claimed to offer certain advantages.[220]

In the process developed by the Dow Chemical Co., of Midland, Michigan, an emulsion of chlorobenzene and 10-20% caustic soda solution is pumped at 5000–6000 lbs. pressure through steel pipes (about 1 in. diameter), which are heated by the outgoing sodium phenolate solution, flowing through an outer tubular system, the temperature thus rising to 350–400°. The optimum temperature is 374°. From this heat-exchange system the emulsion passes through another length of steel pipe which is the reactor; the reaction is exothermic and no further heating is required.[221] No catalyst is necessary. The rate of flow and the length of the coils are such that the reaction is complete in about 30 minutes. The cooled sodium phenolate solution is then extracted with benzene or diisopropyl ether to remove diphenyl ether ($PhCl + PhONa \longrightarrow PhOPh + NaCl$), of which as much as 15% may be present. The addition of about 12% of diphenyl ether based on the weight of chlorobenzene prevents formation of this by-product.[222] The phenol is liberated by hydrochloric acid, and the product fractionated (nickel condenser and nickel-lined receivers) to separate pure phenol from *o*- and *p*-hydroxydiphenyl, which may be recovered in a yield of about 10%. The entire process is carried out as a continuous system, and the design, fabrication, and operation of the plant represent chemical engineering skill of the highest order.

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[218] Phenol manufacture in Germany by various processes has been described by Krieble, Holmes and Wilcoxon, Hobart Pub. Co., Washington D.C., 1947.

[219] See also Rhodes, Jayne, and Bivins, *Ind. Eng. Chem.* **19**, 804 (1927); Tyrer, USP 2,451,996.

[146] See p. 89.

[220] Othmer and Leyes, *ibid.* **33**, 158 (1941).

[221] Putnam, USP 1,921,373.

[222] Hale and Britton, USP 1,607,618.

The IG make phenol at Leverkusen by the Dow process[223, 146] and at Ludwigshafen by the Raschig process.[224, 225, 226] In the latter, which is also operated by Durez Plastics at North Tonawanda, New York, phenol is produced in two stages: (1) $C_6H_6 + HCl + 1/2\ O_2 \longrightarrow C_6H_5Cl + H_2O$; (2) $C_6H_5Cl + H_2O \longrightarrow C_6H_5OH + HCl$. A mixture of benzene, air, and hydrogen chloride is passed through a catalytic furnace containing aluminium-copper-iron hydroxide at 200°, cooling being necessary to keep the temperature constant in the exothermic reaction. The product, which contains 5–20% of chlorobenzene, 0.25–4% of dichlorobenzenes, and 95–76% of benzene, is fractionated, and the recovered benzene is recycled. Chlorobenzene vapor and superheated steam are passed through a second catalytic chamber containing tricalcium phosphate at 450–500°, when an 8–15% conversion with an 85–95% yield of phenol takes place. The product is scrubbed successively with chlorobenzene and water to give (*a*) aqueous hydrochloric acid containing traces of phenol, (*b*) a constant-boiling mixture of steam and chlorobenzene, and (*c*) an aqueous solution of phenol ; (*b*) is recycled and phenol is isolated from (*c*) by extraction with benzene. The IG plant at Ludwigshafen appears to have had to close down because of serious corrosion difficulties, but a larger plant built at Tonawanda, New York, is stated to be working satisfactorily.[227]

Phenol is used in much larger quantities for the manufacture of phenol-formaldehyde resins (Bakelite) than as a dye intermediate. An important use for phenol is in the manufacture of adipic acid from which nylon is made; phenol is catalytically hydrogenated to cyclohexanol, which is also valuable as a solvent; and cyclohexanol is then oxidized to adipic acid.[228]

***m*-Cresol** and ***p*-cresol** are difficult to obtain pure from coal tar, and they are manufactured from the corresponding toluidine by diazotization and hydrolysis.[6] Thus *m*-toluidine is diazotized at −7° with 34% sulfuric

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[223] *BIOS* **664.**

[146] See p. 89.

[224] Mathes, *Angew. Chem.* **52,** 591 (1939); USP 1,964,768.

[225] *BIOS* **507.**

[226] A continuous process for the manufacture of phenol from chlorobenzene has been described by Lee, *Chem. Eng.* **54,** No. 9, 122, 140 (1947). Crawford has surveyed the developments in the catalytic hydrolysis of chlorobenzene to phenol, and the preparation of chlorobenzene by reacting the by-product hydrochloric acid with benzene in presence of air, *Chem. Eng. News* **25,** 235 (1947).

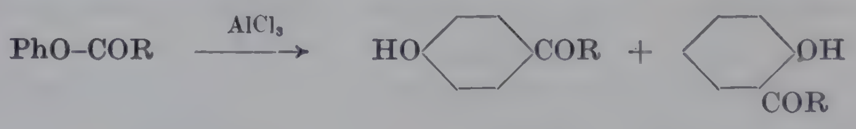
[227] *BIOS* **937.**

[228] For a laboratory preparation of adipic acid, see Ellis, *OSCV* I, p. 18.

[6] See p. 50.

acid and 40% sodium nitrite solution, and the diazo solution is added to a boiling mixture of 30% sulfuric acid and benzene. Boiling is continued for an hour, and after cooling the aqueous layer is saturated with salt; *m*-cresol is recovered from the benzene layer and purified by vacuum distillation. *m*-Cresol is used to make synthetic thymol and menthol. *o*- and *p*-Cresols can be prepared by alkali fusion of the corresponding sodium sulfonates; but the m.p. of *p*-cresol[229] prepared in this manner cannot be raised above 31.4°. Isomeric cresols in *p*-cresol can be detected and removed[230] by treatment with 2,6-dichloroquinone-4-chloroimide, since only phenols with a free *p*-position form indophenols (Hirsch, 1880).

***C*-Alkylphenols** are much less useful as dye intermediates than they are for the preparation of germicides, wetting agents, and plastics, but methods for the *C*-alkylation of phenols, on which hundreds of patents have been taken, will be mentioned briefly. The basic reaction is condensation of a phenol with an alcohol, alkyl halide, or olefin, and among the possible condensing agents are aluminium chloride, zinc chloride, sulfuric acid, and boron trifluoride. Mixtures of *o*- and *p*-alkylphenols are obtained, the alkyl group being secondary or tertiary; *n*-alkyl compounds cannot be prepared by this method since isomerization to the secondary compounds always takes place. *n*-Alkylphenols can be prepared by reduction of the appropriate aryl alkyl ketones, obtained by the Fries reaction[231] (1), the Nencki reaction (2), or the Hoesch reaction (3); the Nencki and Hoesch reactions are applicable to *m*-dihydric phenols, and the former also to α-naphthol. Reduction of the ketones can be effected by the Clemmensen method, with zinc amalgam and boiling hydrochloric acid. Thus the important antiseptic and anthelmintic, 4-*n*-hexylresorcinol, is prepared by a Nencki reaction of resorcinol with acetic acid, followed by reduction.



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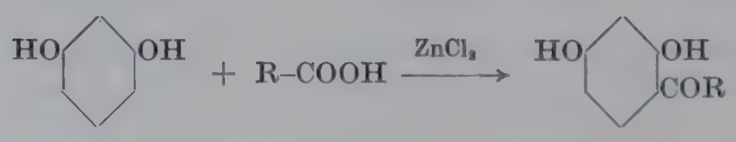

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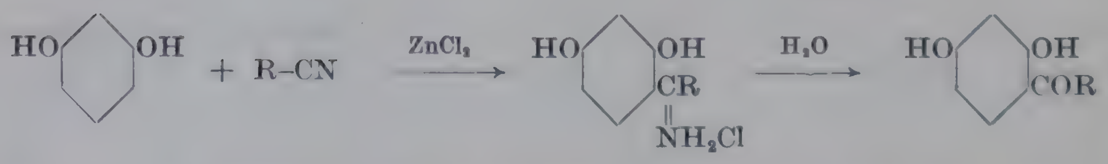

(3)

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[229] Hartman, *OSCV* I, p. 175.

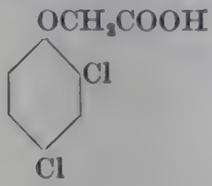
[230] Gibbs, *JACS* **49**, 839 (1927).

[231] The Fries reaction has been reviewed by Blatt, Organic Reactions, I, Wiley, New York, 1942, p. 342–369.

Chlorophenols. *o*- and *p*-Chlorophenols are usually prepared by chlorination of phenol under controlled conditions, and separation of the isomers (*o*- m.p. 8.8°, b.p. 175.6°; *p*- m.p. 43°, b.p. 217°) by fractional distillation. *p*-Chlorophenol can be obtained in 85% yield[232] from *p*-dichlorobenzene when heated with methanolic caustic soda and copper at 225°. *p*-Chlorophenol is an important intermediate for quinizarin.

2,4-Dichlorophenol (m.p. 45°, b.p. 210°) is obtained in about 95% yield by chlorination of phenol below 90° until the setting point is not less than 34° (equivalent to 2.0–2.25 Cl) and purification by fractional distillation.[233, 234] Chlorinated phenoxyacetic acids, especially 2,4-dichlorophenoxyacetic acid (I), have recently come into prominence as selective weed killers, and the chlorination of phenol and the cresols consequently has been studied.[233]

Pentachlorophenol (m.p. 174°, b.p. 309–310°/754.3 mm.) is a largely used fungicide, but is unpleasant to handle on account of its irritant effect on the nose and throat. It is prepared by continued chlorination of phenol, with gradual elevation of the temperature above the setting points of the intermediate chlorophenols until pentachlorination has been effected. Chlorophenols, especially their *C*-alkyl derivatives, are important disinfectants and antiseptics. 6-Chloro-*m*-cresol (II) is prepared technically by chlorination with sulfuryl chloride of the mixture of *m*- and *p*-cresols (60 : 40) obtained from the cresol stills; the *m*-compound is preferentially chlorinated and is separated from unaltered *p*-cresol by fractional distillation. Condensation of (II) with isopropyl chloride in presence of aluminium chloride gives *chlorothymol* (III), a powerful germicide. Another important antiseptic is 2-chloro-*m*-5-xylenol (IV), prepared by chlorination of the appropriate xylenol fraction and purified by crystallization.



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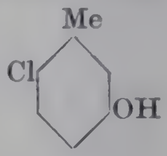

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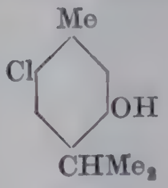

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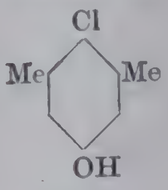

(IV)

Catechol (m.p. 105°, b.p. 240°) is obtained in 91–93% yield by the reaction of *o*-chlorophenol with aqueous caustic soda, barium hydroxide, and cuprous chloride at 200–210° and 18 atm. pressure for 12 hours.[235] Hydrolysis of *o*-dichlorobenzene with aqueous barium hydroxide in presence of a copper catalyst and a reducing agent at 275–285° can also be utilized.[236]

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[232] Kipriyanov *et al.*, *Ukrain. Chem. J.* **7** (Tech.), 78 (1932).

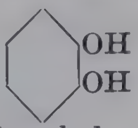
[233] ICI, BP 573,475–9; 573,510.

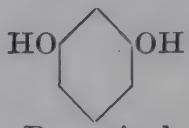
[234] See also Walker and Hayes, *J. Soc. Chem. Ind.* **66**, 215 (1947).

[235] *BIOS* **1154**.

[236] du Pont, BP **425,230**; **432,276**.

The Dakin oxidation of salicylaldehyde with alkaline hydrogen peroxide

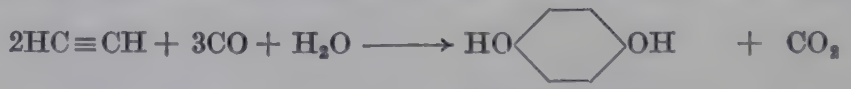

Catechol


Resorcinol

gives catechol in about 70% yield.[237]

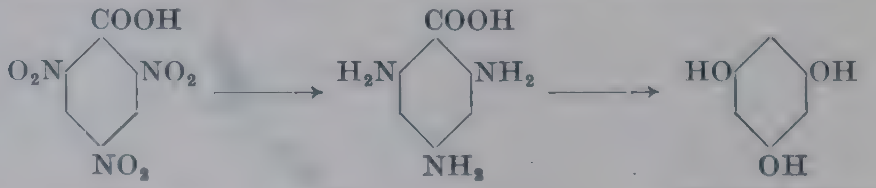
Resorcinol (m.p. 110°, b.p. 281°) is prepared by alkali fusion of disodium benzene-*m*-disulfonate at 320–330° for 8 hours with 5–6 moles of caustic soda under anhydrous conditions. The fusion product is dissolved in water, sodium sulfite filtered off, and the filtrate acidified and boiled to expel sulfur dioxide. The very soluble resorcinol is then extracted with ether or amyl alcohol in a continuous extraction plant. After removal of the solvent the residue is vacuum-distilled. The overall yield from benzene is about 80%. The characteristic test for resorcinol is the formation of fluorescein (yellow solution in aqueous caustic soda with a brilliant green fluorescence) when heated with phthalic anhydride and sulfuric acid. Like phenol, resorcinol forms a triiodo derivative and can be estimated by iodimetry.

Hydroquinone (m.p. 170°), an important photographic developer and also a useful dye intermediate, is prepared by reduction of quinone with sulfurous acid or iron and water at 70–80° or with hydrogen in presence of a nickel catalyst. After filtration of the iron sludge, hydroquinone (98–99.9%) can be obtained by concentration of the clear liquor and evaporation on a drum drier.[238] A remarkable synthesis of hydroquinone developed by the IG involves interaction between carbon monoxide and acetylene in presence of cobalt carbonyl hydride $HCo(CO)_4$.[239]



Hydroquinone

Phloroglucinol (dihydrate, m.p. 117°) is used as a coupler in the manufacture of diazo paper.[41] It is prepared from trinitrotoluene by oxidation to 2,4,6-trinitrobenzoic acid (V) by means of sodium dichromate and concentrated sulfuric acid at 45–55°, reduction of (V) with iron or tin and hydrochloric acid to the corresponding triaminobenzoic acid, and



(V)

Phloroglucinol

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[237] Dakin, *OSCV* I, p. 149.

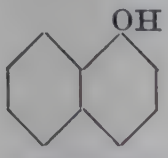
[238] Soc. des usines chimique Rhône-Poulenc, BP 595,514 ; *BIOS* 773.

[239] *BIOS* 355.

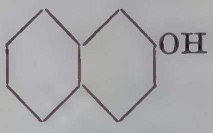
[41] See p. 57.

simultaneous hydrolysis and decarboxylation of the triamine by boiling the dilute hydrochloric acid solution in an atmosphere of nitrogen or coal gas.[240]

α-Naphthol is prepared by hydrolysis of α-naphthylamine with 22% sulfuric acid (1.85 parts) at 180–200° (10 atm. pressure) in a lead-lined autoclave for 8 hours. The collected naphthol is washed free from acid and ammonium sulfate, and purified, if necessary, by vacuum distillation (yield 85–95%).[241] When 1-naphthylamine-5-sulfonic acid (Laurent's acid) is heated with 19% sulfuric acid (one part) at 20 atm. pressure for 24 hours, very pure α-naphthol is obtained.[99] α-Naphthol prepared from the sulfonic acid by alkali fusion is cheaper but liable to contain β-naphthol.[242] The preparation of pure α-naphthol in 90–92% yield from α-chloro- and α-bromonaphthalene by hydrolysis with caustic soda solution under pressure in presence of copper catalysts has been claimed.[243] β-Naphthol present in α-naphthol can be removed as an insoluble calcium compound.[244] α-Naphthol crystallizes in colorless prisms (m.p. 95.8–96.0°, b.p. 288–301°),[245] which turn violet owing to oxidation by air. It is volatile in steam. The sodium salt melts at 44–45°.[246] With nitro compounds such as chlorodinitrobenzene, α-naphthol forms yellow to orange crystalline molecular compounds having fungicidal properties.[247]



α-Naphthol



β-Naphthol

β-Naphthol is a very important intermediate, being indeed the outstanding naphthalene derivative, and is one of the bulk products of the dyestuff industry. The main uses are the production of β-naphthylamine and its derivatives, 2-hydroxy-3-naphthoic acid, and azo dyes formed by coupling with diazonium salts. It has antiseptic and anthelmintic properties, but has the disadvantage of being toxic and irritant. β-Naphthol is prepared[6, 9] by addition of sodium naphthalene-β-sulfonate (28 parts) during 6–8 hours to caustic soda solution (50%; 21.4 parts) which has been evaporated until it has a boiling point of 300°. The temperature is then maintained at 320° for 2 hours. The melt is taken up in water and the naphthol precipitated by sulfur dioxide after filtration of sodium sulfite. The product is purified by vacuum distillation, and the residue of " naphthol pitch " is broken up and used as insulating and jointing material. β-Naphthol crystallizes in colorless plates (m.p. 122.0–122.2°; b.p. 294.85°).[245] It is nonvolatile in steam. Sodium β-napthoxide melts at 120°.[246] β-Naphthol undergoes ready oxidation with ferric chloride to form di-β-naphthol (2,2′-dihydroxy-1,1′-dinaphthyl).[248] Like α-naphthol, it forms molecular compounds with nitro compounds.[244] A simple but important test for the quality of β-naphthol is the clarity of the solution in aqueous caustic soda. As an intermediate for azo and azoic dyes β-naphthol should be free from α-naphthol, which leads to duller shades. The presence of α-naphthol is detected by the blue coloration with ferric chloride; and is quantitatively estimated by coupling the alkaline solution with diazotized *p*-nitroaniline and extracting the dye with caustic soda solution, the β-naphthol dye being insoluble and the α-naphthol dye dissolving to form a deep violet solution.[249] A method of estimating β-naphthol in the absence of other phenols is to treat with excess iodine, β-naphthol forming a triiodo derivative, and to determine the excess of iodine in the usual manner.

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[240] Clarke and Hartman, *OSCV* I, p. 543, 455; Cassella, DRP 102,358. See also Kastens and Kaplan, *Ind. Eng. Chem.* **42,** 402 (1950).

[241] MLB, DRP 74,879; Vorozhtzov and Gutorko, *J. Gen. Chem. U.S.S.R.* **5,** 1518 (1935).

[99] See p. 76.

[242] See, however, National Aniline Co., USP 1,949,243; 1,962,137; 2,025,197.

[243] Dow Chemical Co., USP 1,992,154; 1,996,744; Meyer and Bergius, *Ber.* **47,** 3159 (1914); Chem. Werke Ichendorf, DRP 281,175.

[244] Penn. Coal Prod. Co., USP 1,817,009.

[245] Berliner, Lynch, and May, *JACS* **49,** 1012 (1927).

[246] Meldrum and Patel, *J. Indian Chem. Soc.* **5,** 91 (1928); König, DRP 216,596.

[247] IG, DRP 462,151 ; Buehler, Hisey, and Wood, *JACS* **52,** 1939 (1930).

Like other phenols, the naphthols give characteristic color reactions with bleaching powder and other reagents. The hydroxyl group in α- and β-naphthol is more reactive than in phenol. Thus the naphthols can be O-alkylated by heating with an alcohol and sulfuric acid, essentially as a carboxylic acid is esterified; and the naphthols undergo the Bucherer reaction, being converted into the amines when heated with ammonia and ammonium sulfite solution under pressure. The *ar*-tetrahydronaphthols, in which the unsubstituted ring is reduced, have properties very similar to those of phenols.

Like the naphthylamines the naphthols behave differently from one another on reduction. α-Naphthol gives only *ar*-tetrahydro-α-naphthol (*ar*-α-tetralol; m.p. 68.5–69°) by reduction with sodium and amyl alcohol; hydrogenation in presence of a nickel catalyst gives varying proportions of the *ar*-compound and of tetralin.[250, 251] β-Naphthol gives mainly *ac*-tetrahydro-β-naphthol (alicyclic-β-tetralol; colorless oil, b.p. 264°/716

[6, 9] See p. 50.

[244, 245, 246] See p. 115.

[248] Ioffe, *J. Gen. Chem. U.S.S.R.* **7,** 2710 (1937).

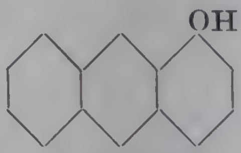
[249] Callan, *J. Soc. Chem. Ind.* **44,** 126T (1925).

[250] Schroeter, *Ann.* **426,** 1 (1922).

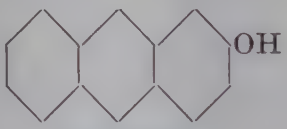
[251] Musser and Adkins, *JACS* **60,** 664 (1938).

mm.) with sodium and amyl alcohol; catalytic reduction gives varying amounts of the two β-tetralols. It is only the *ar*-β-tetralol (m.p. 61.5–62.5°) which has interest as a dye intermediate, and this can be made by hydrogenation of β-naphthol in alkaline solution in presence of a nickel catalyst[252] or by sulfonation of tetralin and alkali fusion of the resultant *ar*-tetrahydronaphthalene-2-sulfonic acid.[253] *Ar*-β-tetralol and its esters have antiseptic and therapeutic properties; *ac*-β-tetralol is an outstanding mosquito repellant.[254]

α- and β-Hydroxyanthracenes (Anthrols) are prepared by reduction of the corresponding anthraquinonesulfonic acid with zinc dust and ammonia to the anthracenesulfonic acid, which is then fused with alkali to yield the anthrol. α-Anthrol is an intermediate for indigoid dyes. 9-Hydroxyanthracene (Anthranol) is mentioned later as a reduction product of anthraquinone.



α-Anthrol



β-Anthrol

α-Hydroxyanthraquinone (Erythroxyanthraquinone, orange needles, m.p. 193°) and β-**hydroxyanthraquinone** (yellow plates, m.p. 302°) are prepared by mild alkali fusion of the corresponding sodium or potassium anthraquinonesulfonate by milk of lime at about 180°. By the ordinary phenol fusion procedure anthraquinone-α-sulfonic acid breaks down into benzene derivatives, and the β-acid gives alizarin.[56] α-Hydroxyanthraquinone yields polyhydroxyanthraquinones by oxidation with oleum. β-Hydroxyanthraquinone occurs naturally in Chay root. An unusual migration of the hydroxyl group in β-hydroxyanthraquinone takes place when a solution is treated with sodium nitrite and boric acid, the product being quinizarin (1,4-dihydroxyanthraquinone). The di- and polyhydroxyanthraquinones are discussed later.[56]

NITROPHENOLS

Phenol is nitrated to a mixture of *o*- and *p*-nitrophenols in a proportion of about 2 : 3 by dilute nitric acid when enough water is added to liquefy crystalline phenol. The careful control of conditions prevents oxidation and tar formation. The presence of a little nitrous acid is necessary, but the reaction does not proceed through an intermediate stage of nitrosation, since *o*-nitrophenol is formed to nearly the same extent as the *p*-compound. Two complexes are apparently formed between phenol and nitrous acid, and these are decomposed oxidatively at different rates.[255] Phenol can also be nitrated in benzene solution by means of nitrogen tetroxide.[256] The isomers are easily separable since the *o*-compound alone is volatile in steam. The preferred method of preparation, however, is hydrolysis of *o*- and *p*-chloronitrobenzene. *p*-Chloronitrobenzene gives *p*-nitrophenol[4] in 99.5% yield when heated with 15% caustic soda solution (4 moles NaOH) for 6 hours at 160°. Other suitable conditions[6] are to heat *p*-chloronitrobenzene with 30% caustic soda solution (1.9 parts) at 95–100° for 12 hours. *o*-Nitrophenol as an impurity in the *p*-compound can be determined by fluorescence analysis after reduction and reaction with benzoic acid.[257] *o*-Nitrophenol crystallizes in yellow needles (m.p. 45°), and *p*- in colorless needles (m.p. 114°). They were formerly employed in the preparation of nitroanisoles and nitrophenetoles, which are now prepared directly from the chloronitrobenzenes. *p*-Nitrophenol has a limited use as an intermediate for sulfur dyes. *m*-Nitrophenol (m.p. 97°) is obtained from *m*-nitroaniline by hydrolysis of the diazonium salt.[258] The important member of this group is 2,4-dinitrophenol (yellow needles, m.p. 114°), the main intermediate for black sulfur dyes; it is formed when 2,4-dinitrochlorobenzene is heated with about eight times its weight of 5% caustic soda solution at 100° for 4–5 hours; a 97% yield is obtainable. A process was described in 1908 by which benzene could be oxidized and nitrated to 2,4-dinitrophenol or to picric acid by a solution of mercuric nitrate in nitric acid,[259] and recently the overall yield in the conversion of benzene into dinitrophenol by this method has been increased to 85%.[260] The mechanism of the reaction, which may be called "oxynitration," involves the following steps:

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[252] IG, BP 468,375.

[253] Schroeter, *Ann.* **426,** 119 (1922).

[254] McKusick, *JACS* **70,** 2196 (1948).

[56] See p. 62.

$$C_6H_6 + Hg(NO_3)_2 \rightleftharpoons PhHgNO_3 + HNO_3;\ PhHgNO_3 + N_2O_4 \longrightarrow PhNO + Hg(NO_3)_2.$$

The nitrosobenzene thus formed can then react in one of two ways:

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[255] Veibel, *Ber.* **63,** 1577, 1582, 2074 (1930).

[256] Staud, Fuess, and Eastman Kodak, USP 1,917,400.

[4] See p. 50.

[6] See p. 50.

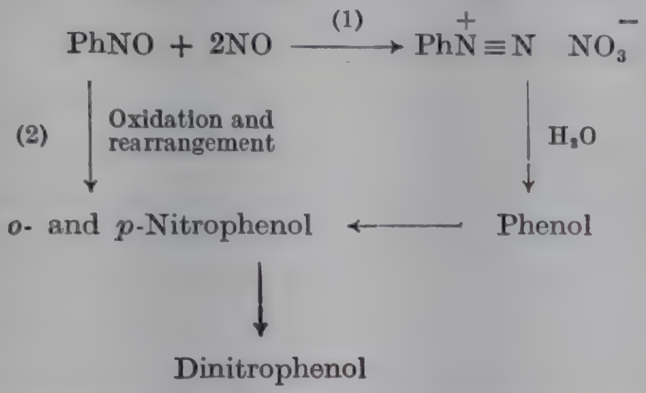
[257] Seaman, Norton and Sundberg, *Ind. Eng. Chem. Anal. Ed.* **12,** 403 (1940).

[258] Manske, *OSCV* I, p. 404.

[259] Wolffenstein and Boeters, *Chem. Abstracts* **2,** 489, 1861 (1908); *Ber.* **46,** 586 (1913).

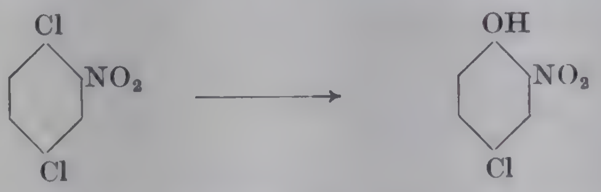
[260] Westheimer, Segel, and Schramm, *JACS* **69,** 773 (1947); Carmack *et al.*, *ibid.* 785; Bachmann *et al.*, *J. Org. Chem.* **13,** 390 (1948); Teeters, Mueller, and Allied Chemical and Dyestuff, USP 2,455,322.

The conversion of nitrosobenzene into phenyldiazonium nitrate, which takes place in good yield when aqueous sodium nitrite is added to basic phenylmercuric nitrate in 20% nitric acid, is an interesting route to diazonium salts.


PhNO + 2NO
(1)
$\mathrm{Ph\overset{+}{N}{\equiv}N\ \ NO_3^-}$
(2)
Oxidation and rearrangement
H_2O
o- and p-Nitrophenol
Phenol
Dinitrophenol

Picric acid (bright yellow plates from water, m.p. 122°), important as an explosive and useful also as a dye intermediate, can be prepared by further nitration of dinitrophenol or by sulfonation of phenol to the disulfonic acid, followed by nitration. The oxynitration of benzene in presence of a mercuric salt catalyst to produce picric acid[261] has been worked out as a practicable procedure in which 1.5 parts of picric acid can be obtained from one of benzene and 1.4 to 1.6 of nitric acid.[262] In a sense picric acid was the first synthetic dye (1799), since it dyes silk and wool directly, but its use was soon abandoned on account of its toxic and explosive character.

When 2,5-dichloronitrobenzene is heated with 6 times its weight of 8% caustic soda solution at 120–130° for 20 hours and the product is acidified,



(I)

4-chloro-2-nitrophenol (I; yellow prisms, m.p. 87°) is obtained.

The various nitrocresols[263] and nitroxylenols[264] have been described, but they are not useful as dye intermediates with one or two exceptions, such as 3-nitro-*p*-cresol. Mononitration of resorcinol yields 4-nitroresorcinol (m.p. 122°), together with a little 2-nitroresorcinol (m.p. 85°);[265] the dimethyl ether of the former is used as a dye intermediate, but it is prepared from 2,4-dichloronitrobenzene. 2,4,6-Trinitroresorcinol (styphnic acid, yellow needles, m.p. 179–180°) is an explosive substance, useful in the laboratory for characterization of aromatic hydrocarbons and alkaloids with which it forms molecular complexes. It is prepared by the mixed acid nitration of resorcinol in one operation or through dinitroresorcinol.[266]

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[261] Wolffenstein and Boeters, DRP 194,883 (1906); USP 923,761.

[262] Aristoff *et al.*, *Ind. Eng. Chem.* **40**, 1281 (1948).

[263] Clemence and Raiziss, *J. Am. Pharm. Assoc.* **23**, 236 (1934).

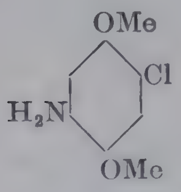
[264] Rowe *et al.*, *J. Soc. Chem. Ind.* **49**, 469T (1930); **50**, 79T (1931).

[265] IG, DRP 633,982; Hodgson and Dyson, *JCS* 946 (1935).

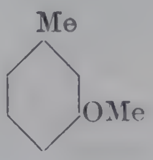
2,4-Dinitro-1-naphthol is a moth-proofing agent and its 7-sulfonic acid is an acid dye, Naphthol Yellow S.[267]

ARYL ETHERS AND THEIR DERIVATIVES

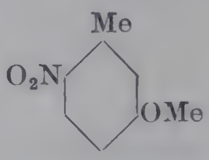
Introduction of methoxyl and ethoxyl groups is a simple method for altering the color of dyes towards blue, and derivatives of anisole, phenetole, tolyl ethers, and hydroquinone dimethyl ether are therefore important intermediates. The general method by which these aryl ethers are prepared is to heat the phenol in alkaline solution with the alkyl chloride or dialkyl sulfate. Thus anisole (b.p. 154°) is obtained[6, 268] in 94% yield by heating phenol (5 parts), 17.5% caustic soda solution (15 parts), and methyl chloride (3.6 parts) at 125° in an autoclave for 5 hours. The neutral oil is separated, washed with caustic soda solution, and purified by vacuum distillation. Hydroquinone dimethyl and diethyl ethers (m.p. 56° and 71.2° respectively), obtained from hydroquinone in a similar manner, are nitrated (34% nitric acid at 35–85°) and reduced to 2-aminohydroquinone dimethyl and diethyl ether (m.p. 81° and 86.7° respectively), which are intermediates for Fast Blue RR and BB Base.[129] The action of sulfuryl chloride on hydroquinone dimethyl ether at 50–55° leads to the 2-chloro compound, which on nitration with 25% nitric acid at 70° gives 2-chloro-5-nitrohydroquinone dimethyl ether; and reduction in solvent naphtha solution with iron and common salt solution yields 2-chloro-5-aminohydroquinone dimethyl ether (I). *m*-Tolyl methyl ether (II), prepared from *m*-cresol, is used for nitration to (III) by 48% nitric acid in carbon tetrachloride, followed by reduction to the amine (IV) with iron and boiling water in presence of a little formic acid.[6] This method of reduction, in which hydrolysis of the *O*-alkyl group is avoided, is generally applicable to the nitroaryl ethers.



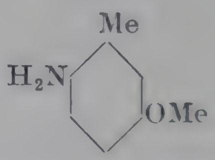
(I)



(II)



(III)



(IV)

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[266] Wilkinson, USP 2,246,963; Jones and Roberts, USP 2,301,912.

[267] See Chapter X.

[6] See p. 50.

[268] See also Hiers and Hager, *OSCV* I, p. 58.

[129] See p. 83.

The *o*- and *p*-chloronitrobenzenes are converted into nitroanisoles, nitrophenetoles, and other nitroaryl ethers in excellent yield by the action of the appropriate alcohol in presence of alkali. The optimum conditions of temperature, alkali concentration, and additions limiting formation of by-products such as azoxybenzenes have been extensively investigated in view of the importance of the nitroaryl ethers as intermediates. Careful control of temperature and of the alkalinity[269] by gradual addition of caustic soda are factors which lead to high yields of the nitroaryl ethers.[270, 271] It is stated[4] that a quantitative yield is obtained from the reaction of the chloronitrobenzene with alcoholic potash at an initial temperature of 50° which is then increased gradually during 5 hours to 80°, with addition of potassium sulfite at regular intervals; the temperature is then maintained at 80° for 25–30 hours. A mixture of manganese dioxide and cobaltic oxide[272] or the former alone[271] is a useful catalyst. Formation of azoxy compounds can be avoided by air passed into the reaction mixture.[10, 13, 273]

o- and p-Nitroanisoles (m.p. 10° and 54°, respectively) are prepared technically by heating the chloronitrobenzene (1 part) with methanol (0.3–0.4 parts) and a 13.5% solution of caustic soda in methanol (1.8 parts) at 70–95° until the reaction is complete as shown by the m.p. of a sample worked up and examined. The yield is over 90%. The corresponding anisidines are obtained by reduction, with iron and aqueous formic acid for the *o*-compound and with 23% sodium sulfide solution at 115° for the *p*-. Nitrophenetoles and phenetidines are prepared in a similar manner.

When acet-*o*-anisidide is nitrated with mixed acid at 25–40°, the reaction being initiated by sodium nitrite and controlled by addition of sodium bisulfite during the progress of the nitration, a mixture of 4- and 5-nitro compounds is obtained.[274] The product is hydrolyzed by 25% sulfuric acid at 95°, and on neutralization of part of the acid and dilution, the less basic 5-nitro-*o*-anisidine (Fast Red B Base) separates (65% yield). From the filtrate, the 4-nitro compound (Fast Scarlet R Base) can be recovered

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[269] du Pont, USP 2,038,620; 2,056,260–1.

[270] Richardson, *JCS* 522 (**1926**); *J. Soc. Chem. Ind.* **45**, 200T (1926); McCormack and Stockmann, *Ind. Eng. Chem.* **31**, 278 (1939).

[271] Dey, Govindachari, and Udupa, *J. Sci. Ind. Res.* (*India*) **4**, 369 (1945); **5**, 25. 37 (1946).

[4] See p. 50.

[272] Aoyama and Nanai, *J. Pharm. Soc. Japan* **53**, 613 (1933).

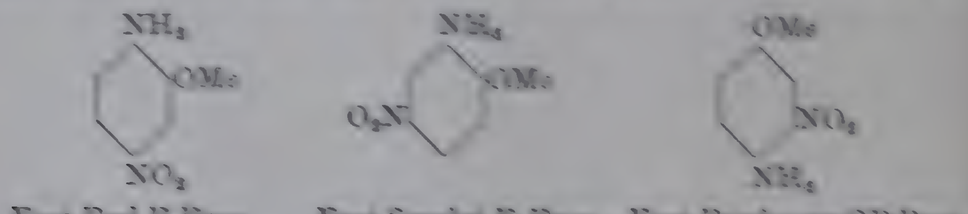
[10] See p. 50.

[13] See p. 50.

[273] *BIOS* **116.**

[274] For a study of the nitration of *o*-alkoxyaniline and *o*-alkoxyacetanilide, see Verkade *et al., Rec. trav. chim.* **66**, 374 (1947).

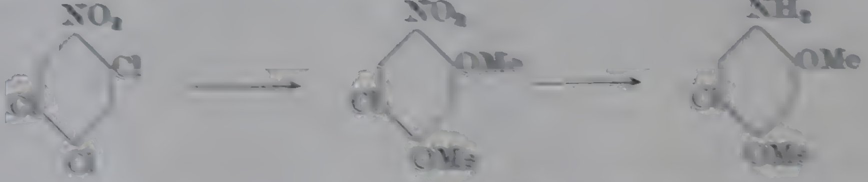
(23% yield). The latter can also be prepared in 82% yield by treatment of *o*-anisidine at 35–40° with dilute nitric acid with formation of the nitrate, which is then converted into the 4-nitro compound by addition to 93%



Fast Red B Base Fast Scarlet R Base Fast Bordeaux GP Base

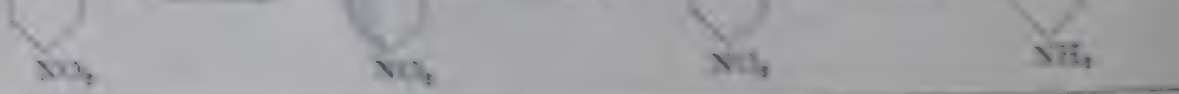
sulfuric acid at 0–5°.* Nitration of acet-*p*-anisidide in chlorobenzene solution with 62% nitric acid followed by hydrolysis of the acetyl group with 5% caustic soda solution at 75° gives 3-nitro-*p*-anisidine, or Fast Bordeaux GP Base (m.p. 129°), in nearly quantitative yield.[275] 3-Nitro-*p*-phenetidine (Fast Blue Red O Base; m.p. 113°) is prepared by similar reactions.

4-Nitroresorcinol dimethyl ether (m.p. 76–77°) can be prepared from 2,4-dichloronitrobenzene in the same manner as the nitroanisoles from the nitrochlorobenzenes; reduction of the nitro compound in benzene solution by means of iron and aqueous formic acid gives 4-aminoresorcinol dimethyl ether (m.p. 32.5–33.5°). The action of methanolic caustic soda on 2,5-dichloronitrobenzene at 90° gives 4-chloro-2-nitroanisole (yellow needles, m.p. 98°), which on reduction gives 4-chloro-*o*-anisidine (m.p. 84°). When 2,4,5-trichloronitrobenzene is heated with about thrice its weight of 10% methanolic caustic soda, first under reflux for a few hours and finally at 90° under pressure, the product is 4-chloro-6-nitroresorcinol dimethyl

 (V)

ether (m.p. 123.5°), reduction of which with boiling sodium hydrosulfide solution gives 4-chloro-6-aminoresorcinol dimethyl ether (V).†

4-Amino-2-methoxytoluene (VI) is used† for making Fast Brown V Base. 3-Amino-4-methoxytoluene (VII) ("Cresidine"; m.p. 51.5°, b.p.

 (VI)

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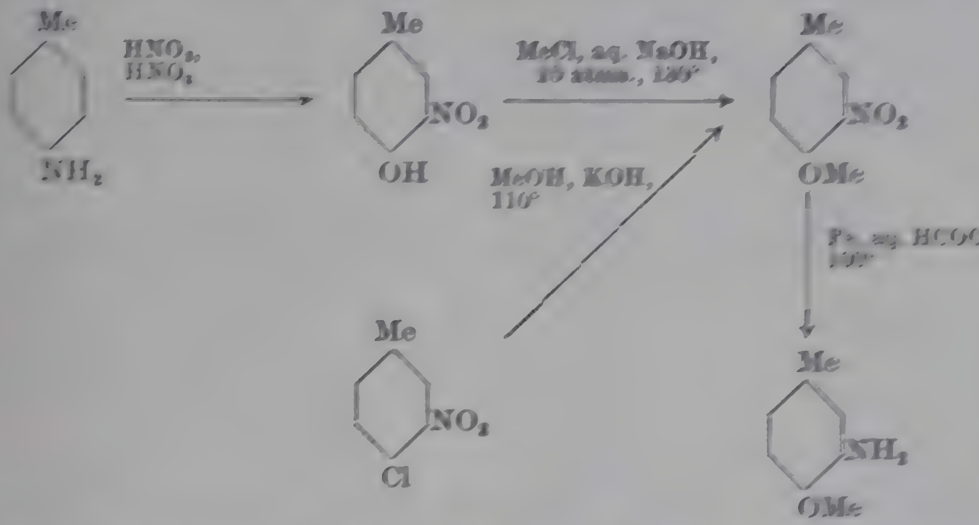
* See p. 108.

[275] See also Fanta and Tarbell, *Org. Syntheses* 25, 78 (1945).

† See p. 60.

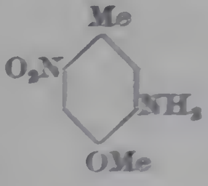
235°; volatile in steam) is an important intermediate for violet and blue azo dyes. It is usually prepared from *p*-toluidine by the indicated series of reactions; but IG used the by-product 4-chloro-3-nitrotoluene. 3-Amino-4-ethoxytoluene is a minor intermediate, prepared[4] from *p*-cresol or from

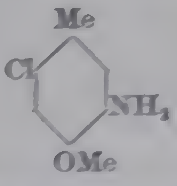

Me
NH₂
HNO₂,
HNO₃
Me
NO₂
OH
MeCl, aq. NaOH,
MeOH, KOH,
110°
Me
NO₂
Cl
Me
NO₂
OMe
HCOOH,
Me
NH₂
OMe

(VII)

p-toluidine as in the case of (VII) and used in making Fast Black G Salt for azoic dyeing.[129] Cresidine (VII) gives the 6-nitro compound (VIII) by acetylation of the amino group, nitration and deacetylation;[5] (VIII) is

(VIII)

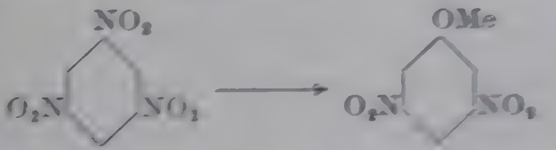

Me
O₂N
NH₂
OMe

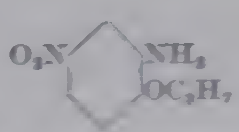

Me
Cl
NH₂
OMe

(IX)

used in making the printing color, Rapidogen Red Violet RR.[129] Chlorination of (VII) by means of sulfuryl chloride, or of the acetyl derivative by chlorine in chlorobenzene solution and subsequent deacetylation, gives (IX) used in making Naphtol AS-L3G.[129]

An interesting example of the replacement of a nitro group by an alkoxy group is the preparation of 3,5-dinitroanisole (m.p. 105–106°) in


NO₂
O₂N
NO₂
OMe
O₂N
NO₂


O₂N
NH₂
OC₃H₇

(X)

about 70% yield by heating 1.3.5-trinitrobenzene with sodium methoxide in methanol.[276]

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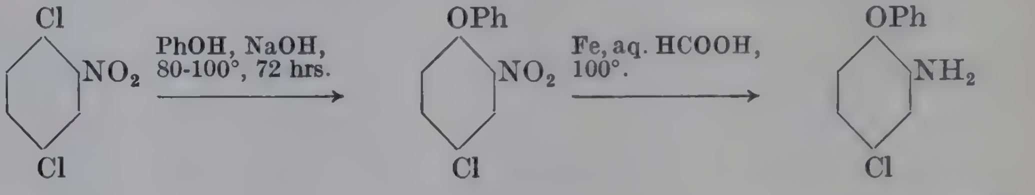
[3] See p. 50.

[4] See p. 83.

[5] de Bruyn (1890); Reverdin, OSCV I, p. 219.

2-Propoxy-5-nitroaniline (X) is a sweetening agent (4000 times sweeter than sugar). It is prepared by separating it from the isomeric 4-propoxy-3-nitroaniline, both being obtained by reduction of 2,4-dinitrophenyl propyl ether.[277]

Aminodiphenyl ethers are useful for bright red azo and azoic dyes. Examples are *o*-aminodiphenyl ether and its 4-chloro and 4,4′-dichloro derivatives (Fast Red FG Base and Fast Red FR Base). Careful temperature control during the condensation of phenol with the dichloronitrobenzene is necessary to avoid explosion.[8, 10, 278]



Fast Red FG Base

Methyl, ethyl, and butyl ethers of β-naphthol are used under the name "nerolin" in the perfumery industry for production of orange and strawberry odors. They are prepared, like the esters of carboxylic acids, by heating β-naphthol with the appropriate alcohol in presence of sulfuric acid or hydrogen chloride. A derivative of a β-naphthyl ether, which is important as a dye intermediate, is 2-ethoxy-1-naphthylamine-6-sulfonic acid, mentioned later among the aminonaphtholsulfonic acids. Alkoxy- and aryloxyanthraquinones can be prepared from the reaction of the sulfonic acids or nitro compounds or chloro or bromo compounds with potassium alkoxides or aryloxides at about 200°, copper being as usual a suitable catalyst for the replacement of halogen. Thus 1,5-diphenoxyanthraquinone, an intermediate for 4,8-diamino-1,5-dihydroxyanthraquinone, is prepared by heating disodium anthraquinone-1,5-disulfonate with sodium phenolate. An aryloxy group in the α-position can be replaced by an alkoxy group[279] by reaction with alcoholic potassium hydroxide at 80°.

BENZIDINE AND SIMILAR DIAMINES

While the reduction of nitrobenzene with metal and acid gives aniline, a variety of other compounds can be obtained by electrolytic, neutral, or alkali reduction (Chart 5). Careful study of the electrolytic process (Haber,

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[277] Polak and Schwarz's Essencefabrieken, DP 52,980 ; 57,133 ; 59,306 ; 59,313.

[8] See p. 50.

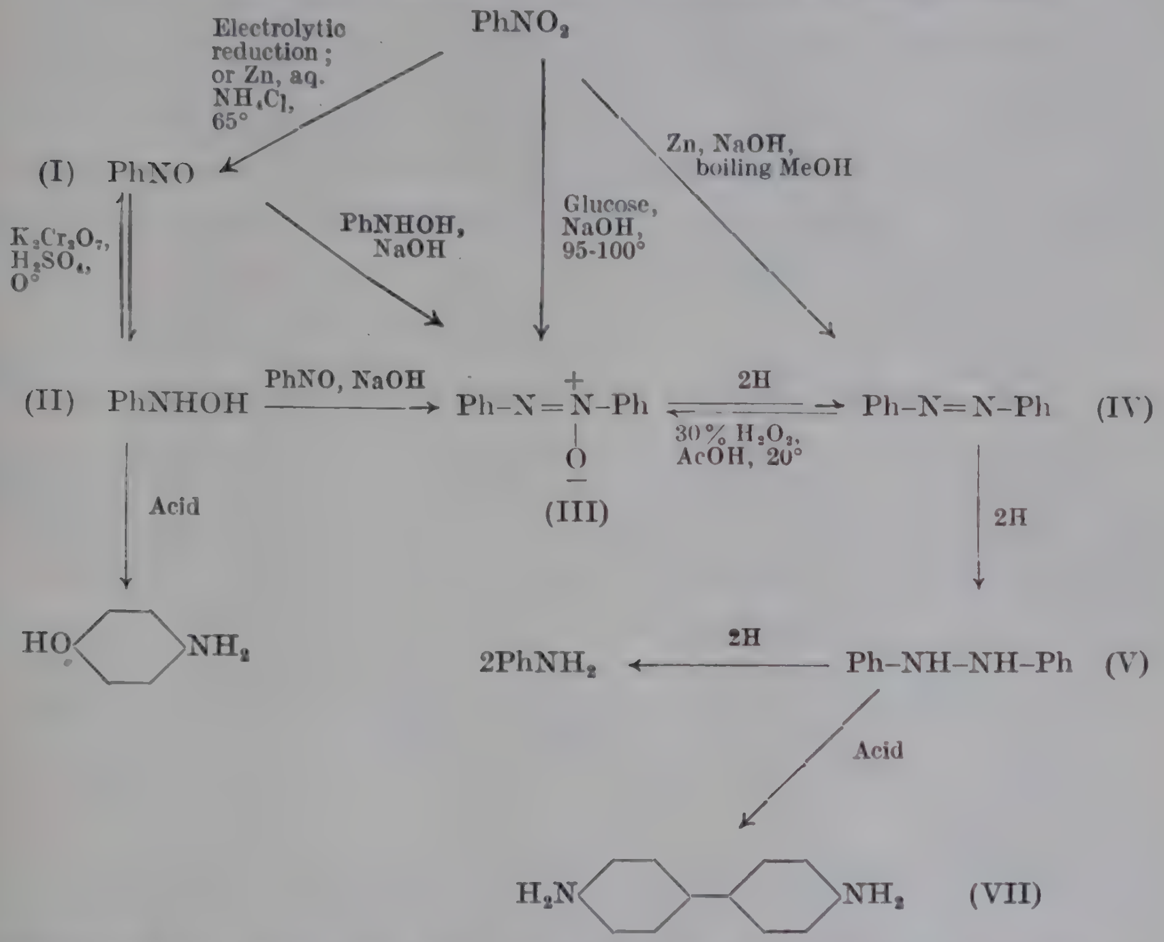
[10] See p. 50.

[278] The preparation of *p*-nitrodiphenyl ether is described by Brewster and Groening, *OSCV* II, p. 445.

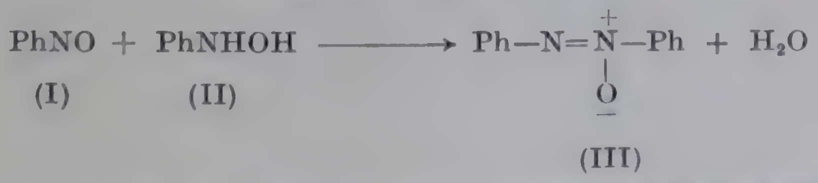
[279] IG, DRP 538,014.

CHART 5

REDUCTION AND REARRANGEMENT PRODUCTS OF NITROBENZENE


PhNO₂
Electrolytic reduction; or Zn, aq. NH₄Cl, 65°
(I) PhNO
Zn, NaOH, boiling MeOH
Glucose, NaOH, 95-100°
PhNHOH, NaOH
K₂Cr₂O₇, H₂SO₄, 0°
(II) PhNHOH
PhNO, NaOH
Ph–N=N–Ph
O
(III)
2H
30% H₂O₂, AcOH, 20°
Ph–N=N–Ph (IV)
Acid
2H
HO NH₂
2PhNH₂
2H
Ph–NH–NH–Ph (V)
Acid
H₂N NH₂ (VII)

1900)[280, 281] has shown that the first stage is formation of nitrosobenzene (I),[282] which on account of its good depolarizing properties immediately undergoes further reduction to phenylhydroxylamine (II).[283] Under alkaline conditions (I) and (II) condense to form azoxybenzene (III). Further reduction, which may be effected by allowing the electrolytic



$$\underset{\text{(I)}}{\text{PhNO}} + \underset{\text{(II)}}{\text{PhNHOH}} \longrightarrow \underset{\text{(III)}}{\text{Ph—N=}\overset{+}{\underset{\underset{-}{\text{O}}}{\text{N}}}\text{—Ph}} + \text{H}_2\text{O}$$

---

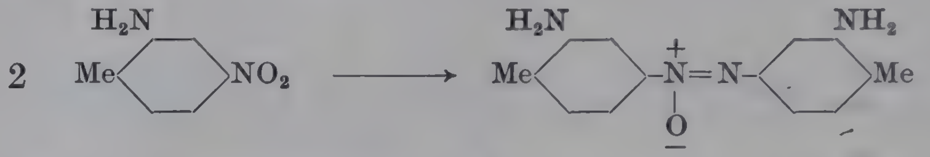
[280] For details see Glasstone and Hickling, Electrolytic Oxidation and Reduction, Chapman and Hall, London, 1935.

[281] Dey, Govindachari, and Rajagopalan, *J. Sci. Ind. Res.* (*India*) **4,** 559, 569, 574, 636, 642, 645 (1945); **5,** 75, 77 (1946).

[282] For the preparation of nitrosobenzene by the oxidation of phenylhydroxylamine with sodium dichromate and sulfuric acid, see Coleman, McCloskey, and Stuart, *Org. Syntheses* **25,** 80 (1945).

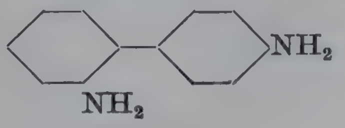
[283] Phenylhydroxylamine can be prepared (Kamm, *OSCV* I, p. 446) in 62–68% yield by the reduction of nitrobenzene with zinc dust and water in presence of ammonium chloride at 60–65°. A laboratory use for phenylhydroxylamine is the preparation of cupferron [PhN(NO)ONH$_4$], a reagent for copper and iron; Marvel, *ibid.* p. 177.

reaction to proceed or by treatment of (III) with iron and water, leads to azobenzene (IV) and to hydrazobenzene (V); (III) (yellow, m.p. 36°),[284] (IV) (orange red, m.p. 68°),[285] and (V) (colorless, m.p. 126°) can be prepared directly from nitrobenzene in yields of 70–90% under conditions such as those indicated in the chart. Thus the diaminoazoxytoluene (VI; yellow needles, m.p. 168°) used for making the disazo dye Rosophenine is obtainable in good yield on reduction of 4-nitro-o-toluidine with an alkaline solution of sodium stannite at about 95°.

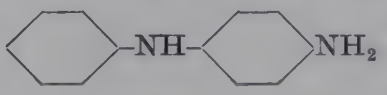


(VI)

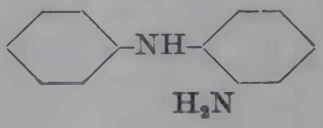
Acid induces a transformation of hydrazobenzene (V) into benzidine (VII); by-products of the reaction are 2,4′-diaminodiphenyl (VIII), 4-aminodiphenylamine (semidine; IX), and 2-aminodiphenylamine (o-semidine; X). 2,2′-Diaminodiphenyl (o-benzidine) is not formed from hydrazobenzene, but such o,o′-compounds are formed in good yield in the naphthalene series. The formation of these by-products depends on the conditions of the reaction and on the substituents present in the hydrazobenzene molecule, and the " benzidine transformation " has been extensively studied with regard to these factors and the mechanism of the rearrangements.[286, 287] With hydrazobenzene itself benzidine can be produced in excellent yield, but significant quantities of (VIII) are formed.



(VIII)

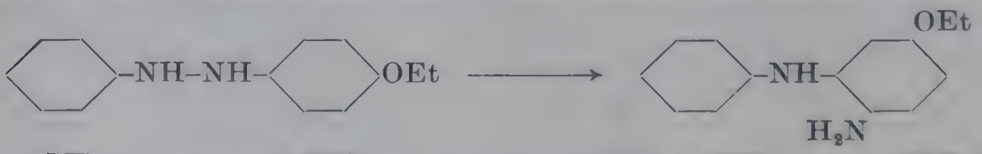


(IX)

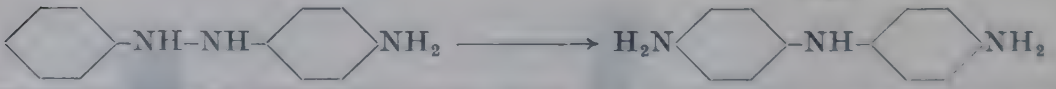


(X)

p-Substitution favors the semidine change (formation of derivatives of IX and X; e.g., XI and XII); the commercial method for the preparation



(XI)



(XII)

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[284] The preparation of azoxybenzene by reduction of nitrobenzene with alkaline sodium arsenite is described by Bigelow and Palmer, *OSCV* II, p. 57. For the preparation of azobenzene-4-carboxylic acid by the condensation of nitrosobenzene with p-aminobenzoic acid, see Anspon, *Org. Syntheses* **25**, 86 (1945).

[285] For the preparation of azobenzene, see Bigelow and Robinson, *Org. Syntheses* **22**, 28 (1942).

[286] Jacobson *et al.*, *Ann.* **428**, 76 (1922); Robinson, *JCS* 220 (**1941**); Hughes and Ingold, *ibid.* 608.

[287] Dewar, *ibid.* 777(**1946**); Hammick and Mason, *ibid.* 638 (**1946**); *ibid.* 1939 (**1949**); Hammond and Shine, *JACS* **72**, 220 (1950); Carlin and Forshey, Jr., *ibid.* 793.

of (XII) is different, however, and is mentioned later. Certain *p*-substituents, such as Cl, COOH, and SO_3H, are ejected during the reaction. The formation of benzidine does not proceed through semidine, since the latter is not converted into benzidine by treatment with acid.[288] Fission into the free radicals $ArNH^{\cdot}$ is also not involved, as shown by the fact that the action of acid on a mixture of 2,2′-dimethoxy- and diethoxyhydrazobenzene yields solely the two symmetrical benzidines and no methoxyethoxybenzidine.[289] An intramolecular change apparently takes place.

Processes for the manufacture of benzidine. Three processes are in vogue for the manufacture of hydrazobenzene. (1) The simplest and most widely used process[6] is the reduction of nitrobenzene with zinc and aqueous caustic soda.[290] In a typical zinc reduction 50% caustic soda solution (7 kg.) is added to a mixture of nitrobenzene (80 kg.), zinc dust (320 kg.) and solvent naphtha (400 kg.) at 105°. The temperature rises to 125°, at which it is maintained by the gradual and alternate addition of nitrobenzene (170 kg.) and caustic soda solution (20 kg.). The batch is now in the azobenzene stage, and reduction to hydrazobenzene is effected by addition of zinc dust (80 kg.) and water (25 l). The temperature is reduced to 110°, and agitation continued, until the reaction subsides and a spot on filter paper is colorless. More solvent naphtha (300 kg.) is added, together with water (100 l.) to convert the zinc oxide into the coarse and more readily filterable hydroxide. The naphtha solution is run out through the zinc hydroxide bed, which is reextracted with more naphtha; zinc oxide is recovered by calcining the hydroxide and sold for the preparation of lithopone. A technique for the separation of zinc oxide produced in the zinc reduction of nitro compounds is to wash the reduction product on screens having perforations smaller than the hydrazo compound but larger than the zinc oxide.[291] The combined naphtha solutions of hydrazobenzene from two batches are then submitted to the benzidine change by treatment with water (100 l.), 40% sodium bisulfite solution (30 kg.), and 19% sulfuric acid (1260 kg.) at a temperature of 20–25° for 8 hours. In one IG process, the reaction mixture is alkalized with concentrated sodium carbonate solution, the naphtha layer separated, washed, and cooled, when benzidine separates as the free base, which is collected on a vacuum filter and purified by vacuum distillation. The distilled base is blown to cooling trays, solidified, and ground.

(2) Sodium amalgam and alcohol are used for reduction.[292]

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[288] Robinson and Robinson, *JCS* **113**, 645 (1918).

[289] Ingold and Kidd, *ibid.* 984 (**1933**).

[6] See p. 50.

[290] See also du Pont, USP 2,175,244; 2,194,938; BP 518,985; Hallie, USP 2,486,358.

[291] Shebwev, RP 66,877.

[292] Poma and Pellegrini, DRP 410,180.

(3) There are numerous patents on the electrolytic reduction of nitrobenzene to hydrazobenzene either in a solvent such as alcohol or as an alkaline emulsion.[293, 281] A notable advance is the use of a concentrated solution of sodium and potassium arylsulfonates (e.g., xylenesulfonates) as a solvent for nitrobenzene,[294] but Dey *et al.* have shown that reduction in 10% alkaline emulsion at an iron cathode, on which spongy lead is deposited, is superior to other methods of electrolytic reduction. They have described a small-scale plant suitable for industrial application, in which a 92% yield of hydrazobenzene is obtainable under optimum conditions.

Hydrazobenzene can be estimated by addition of an excess of Bindschedler's Green,[141] which is its own indicator, and back titration with titanous sulfate.[287]

Benzidine crystallizes from water in large silky plates, m.p. 127.5–128°. The free base is highly toxic, for it produces bladder tumors, and handling must be completely avoided. In fact, "in our present state of knowledge the manufacture of benzidine should be regarded integrally as a hazard from start to finish, and the base should be prepared only if the plant design is such as to preclude absolutely any maintained contact with, or exposure to, dust of the final product."[169] For the preparation of azo dyes, it is best to use directly the solution of the hydrochloride, the form in which benzidine is obtained by treatment of hydrazobenzene with hydrochloric acid. Benzidine was used at one time in azoic dyeing under the name Fast Corinth B Base. A characteristic reaction of benzidine is the formation of a dark blue precipitate (XIII), analogous to the Wurster dyes from *p*-phenylenediamine and its derivatives, on addition of potassium dichromate to an acid solution. Possessing two amino groups, benzidine can be doubly diazotized and coupled to form disazo dyes, which have the special property of dyeing cellulose without a mordant. Benzidine and some of its simpler derivatives, in which the substituents are *o*- to the amino groups, are therefore intermediates of great importance for the preparation of largely used direct cotton dyes such as Congo Red and Benzopurpurine. Three such derivatives of benzidine are *o*-tolidine (XIV; m.p. 129°; prepared from *o*-nitrotoluene), *o*-dianisidine (XV; m.p. 137°; from *o*-nitroanisole)

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[293] Elbs, *Chem. Ztg.* **17**, 209 (1893).

[281] See p. 125.

[294] McKee *et al.*, *Trans. Am. Electrochem. Soc.* **62**, 203 (1932); **65**, 135, 161 (1934); **66**, 329 (1935).

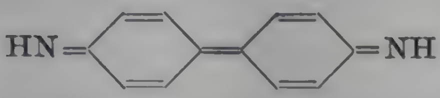
[141] See p. 88.

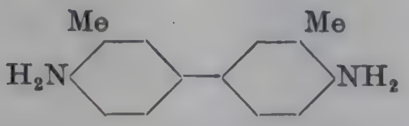
[287] See p. 126.

[169] See p. 95.

and *o*-dichlorobenzidine (XVI; m.p. 133°; from *o*-chloronitrobenzene). These substituted benzidines are prepared[10] by the zinc-alkali method.

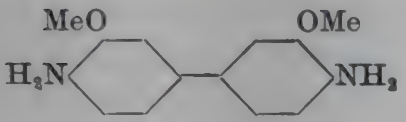
(XIII)

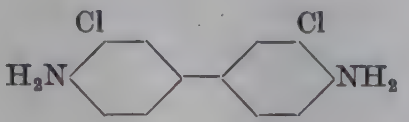




(XIV)

(XV)



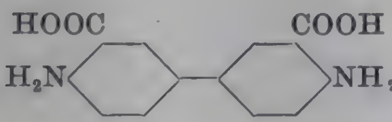


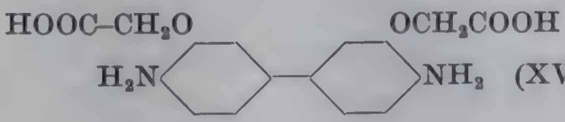
(XVI)

The use of a solvent, such as solvent naphtha, is unnecessary. The benzidine transformation is carried out by means of 10% hydrochloric acid at 0–10° in the case of dichlorobenzidine. The zinc dust treatment of *o*-nitroanisole must be carried out cautiously to avoid too energetic reduction. At the azoxyanisole stage the temperature must be carefully controlled and the batch must be drowned in water if the agitator stops, since azoxyanisole explodes spontaneously at 150°.

Azo dyes prepared with the same coupling components from tetrazotized benzidine, tolidine, and dianisidine are progressively bluer in shade. Tolidine was at one time used in azoic dyeing as Fast Dark Blue R Base, but has now been replaced by an azobenzene derivative; dianisidine is still used to a limited extent as Fast Blue B Base. Benzidine-3,3′-dicarboxylic acid (XVII, from *o*-nitrobenzoic acid) and benzidine-3,3′-diglycollic acid (XVIII, from *o*-nitrophenoxyacetic acid) are useful in the preparation of direct cotton dyes suitable for aftertreatment on the fiber with copper salts.[295] 3,3′-Dihydroxybenzidine (white powder, darkening on exposure to air) can be prepared by demethylation of dianisidine with hydriodic acid[296] or aluminium chloride.[297] Metal complexes of disazo dyes derived from 3,3′-dihydroxybenzidine have been mentioned as direct cotton dyes with good fastness to light and washing.[297, 298] 3-Hydroxy-3′-methoxybenzidine (m.p. 153–154°) can be prepared by prolonged heating of dianisidine with 65% sulfuric acid.[298a]

(XVII)





(XVIII)

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[10] See p. 50.

[295] See Chapter XVII. Cf. Vogt, Marschall, and General Aniline and Film, BP 607,762.

[296] DRP 70,718; see also Burkhardt and Wood, *JCS* 151 (1929).

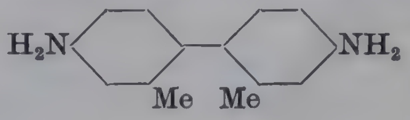
[297] Straub, Brassel, Pieth, and Ciba, USP 2,439,153; Ciba, BP 609,299–609,302.

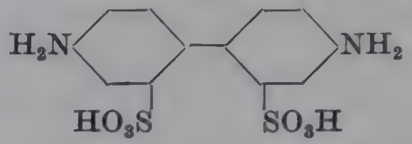
[298] See Chapter XIII.

[298a] Straub, Brassel and Ciba, USP 2,459,467.

A few *m*-benzidines (2,2′-derivatives of diphenyl), such as *m*-tolidine (XIX) and benzidine-*m*-disulfonic acid (XX) prepared respectively from

(XIX)



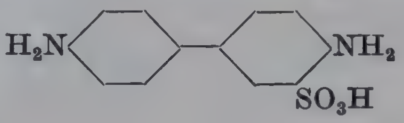


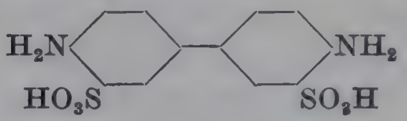
(XX)

m-nitrotoluene and nitrobenzene-*m*-sulfonic acid, are useful as intermediates for dyes which have little or no affinity for cotton but have excellent properties as acid dyes for wool. All these benzidine derivatives are prepared in the same manner as benzidine by reduction of the appropriately substituted nitrobenzene to the hydrazobenzene followed by acid treatment to effect the benzidine rearrangement.

Sulfonation of benzidine gives different products according to the conditions employed. When benzidine sulfate is treated with concentrated sulfuric acid at 210°, the monosulfonic acid (XXI) is first obtained, and then the disulfonic acid (XXII). An 88% yield of the monosulfonic acid can be obtained by treatment of benzidine sulfate in *o*-dichlorobenzene (12 parts) with 65% oleum (0.5 part) at 60°, and continuing the sulfonation with monohydrate (0.25 part) at 180° for several hours.[10] With stronger oleum and higher temperature, benzidine-sulfone (XXIII) and its disulfonic acid (XXIV) are produced. *o*-Tolidine-6,6′-disulfonic acid (XXV) is prepared[10] from 2-nitrotoluene-4-sulfonic acid.

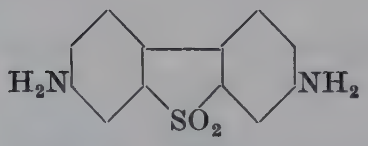
(XXI)

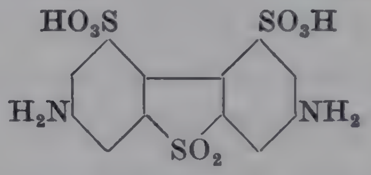




(XXII)

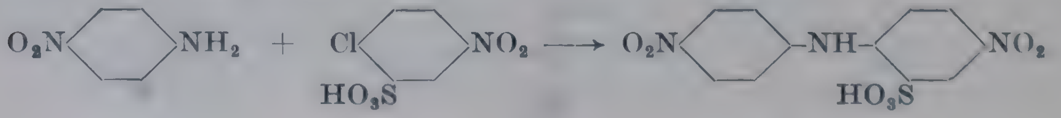
(XXIII)

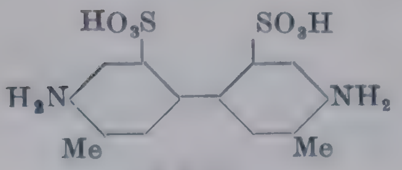




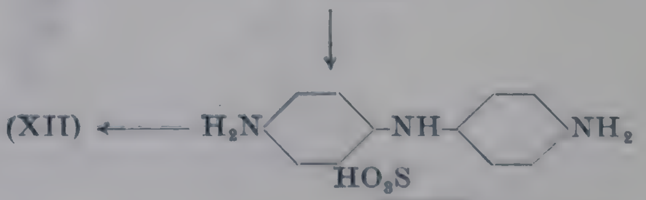
(XXIV)

Other diamines used as intermediates for direct cotton dyes. There are a few *p,p′*- substituted diamines analogous to benzidine which are used for tetrazotizing and coupling with suitable components for making azo dyes substantive to cotton. One example is 4,4′-diaminodiphenylamine (XII; colorless plates, m.p. 158°), mentioned earlier in connection with





(XXV)



(XXVI)

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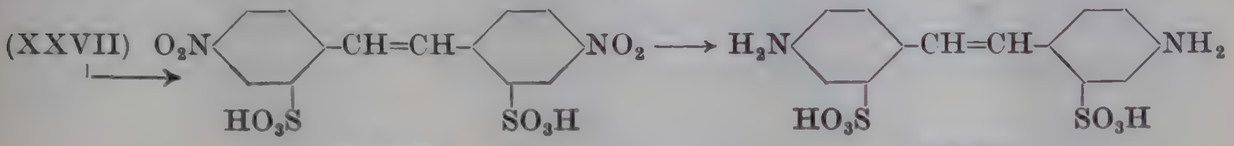
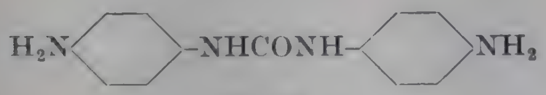
[10] See p. 50.

the semidine change and as the reduction product of the indamine from aniline and *p*-phenylenediamine. The technical method for the preparation of (XII), which is also useful as a Fast Base (Fast Black B Base), is the desulfonation, by boiling with aqueous sulfuric acid, of the sulfonic acid (XXVI), which is obtained by condensing *p*-nitroaniline with 4-nitrochlorobenzene-2-sulfonic acid and reducing the nitro groups. The largely used 4,4′-diaminostilbene-2,2′-disulfonic acid (XXVIII)[299] may be prepared by treatment of an alkaline solution of 4-nitrotoluene-2-sulfonic acid (XXVII) with zinc dust until the deep red color disappears, but the technical method is to oxidize (XXVII) in alkaline solution with air in presence of manganese sulfate as catalyst or with sodium hypochlorite to form (XXIX), which is then reduced with iron and acid;[300] (XXVIII) is an intermediate for the important dye Chrysophenine. The dinitro compound (XXIX) and the monoamine obtained by partial reduction of (XXIX) are even more important intermediates for the preparation of azo dyes of the stilbene class.[299]


(XXIX) (XXVIII)

The urea (XXX), prepared by condensing phosgene with two moles of *p*-nitroaniline and reducing the product, its dicarboxylic acid (XXXI), and its disulfonic acid (XXXII) have limited use; dyes containing the urea group are more usually prepared by phosgenating the simpler azo dyes. 3,3′-Dimethylnaphthidine (XXXIII), which may prove to be of use in the preparation of disazo dyes of the benzidine type, is obtained in 74% yield by direct oxidation of 2-methyl-α-naphthylamine with boiling 66% sulfuric acid. The usual route through a hydrazo compound cannot be used since the reduction of 1-nitro-2-methylnaphthalene yields only 2-methyl-α-naphthylamine.[301]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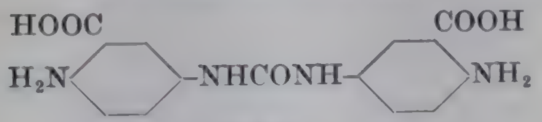
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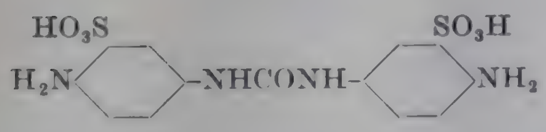
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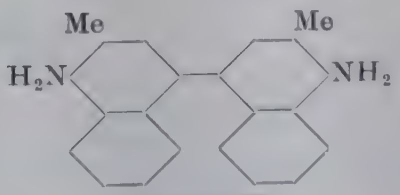
(XXXIII)

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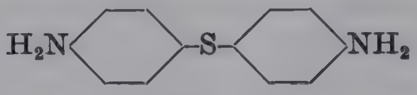
[299] Chapter XX.

[300] *BIOS* 259.

[301] Fierz-David, Blangey and Duebendorfer, *Helv. Chim. Acta* **29**, 1661 (1946).

Diamines used for wool dyes. 4,4′-Diaminodiphenylmethane, 4,4′-diaminodiphenylsulfide (XXXIV, thioaniline) and its 2,2′-disulfonic acid (XXXV) are examples of diamines which on tetrazotization and coupling with suitable components give wool dyes and not direct cotton dyes. Thioaniline (XXXIV), admixed with about an equal part of the *o*-isomer (XXXVI), is obtained in 40% yield when aniline is heated with sulfur and basic lead carbonate [$2PbCO_3,Pb(OH)_2$] at 100° until all the lead has been converted to the sulfide (20 hours).[6] The disulfonic acid (XXXV) is obtained from 4-chloronitrobenzene-3-sulfonic acid. An interesting example of a diamine used for preparing wool dyes is 1,1′-bis-*p*-aminophenylcyclohexane (XXXVII), obtained from the reaction of cyclohexanone with aniline (3.25 parts) and concentrated hydrochloric acid (3.6 parts) at 125° for 10 hours.[10] The analogs from *o*-toluidine and *o*-anisidine are also used.



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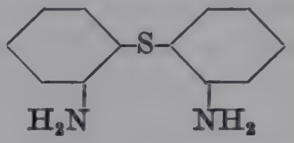
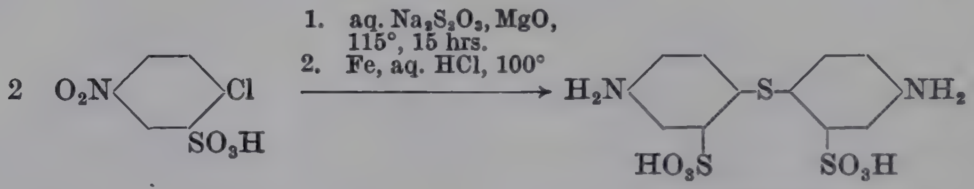


(XXXVI)



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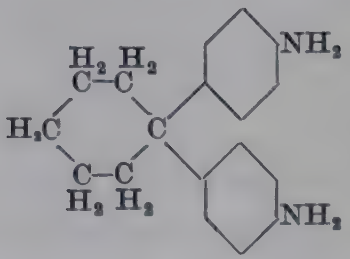

(XXXVII)

DIPHENYL AND ITS DERIVATIVES

Diphenyl is produced technically by passing benzene through molten inorganic salts[302] at 750–800°. The chlorinated diphenyls are useful on account of their waxlike character and their electrical insulating properties. A process for the nearly quantitative conversion of 4,4′-dichlorodiphenyl to benzidine has been described.[303] *o*-Hydroxydiphenyl and chlorinated hydroxydiphenyls are valuable fungicides and bactericides ; the former has also found use as a raw material for plastics; *p*-hydroxydiphenyl is a valuable raw material for varnish resins. Diphenyl can be nitrated to give 2- and 4-nitrodiphenyl and 2,4-dinitrodiphenyl. The amines obtained by reduction, 2,2′-diaminodiphenyl-4,4′-disulfonic acid (prepared by sulfonation, nitration, and reduction of diphenyl), and other diphenyl derivatives might have interest in the future as dye intermediates.[304] Heating of 2,2′-diaminodiphenyl-4,4′-disulfonic acid in aqueous solution with a salt at 180° induces ring closure with formation of carbazole-2,7-disulfonic acid, converted by alkali fusion at 260–280° into 2-hydroxycarbazole-7-sulfonic acid.[305] 2-Aminocarbazole (I) has been synthesized from diphenyl by monosulfonation, trinitration, reduction to (II), cyclization to (III), and desulfonation.[306]

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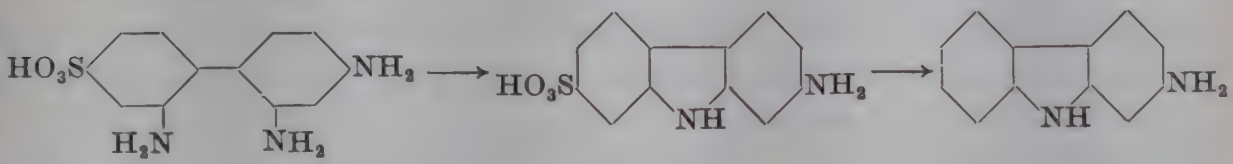
[6] See p. 50.

[10] See p. 50.

[302] *BIOS* 1787; IG, BP 371,335; Swann Research Corp., USP 1,894,283; Warren and Durgin, USP 1,891,514; see also Wibaut *et al.*, *Rec. trav. chim.* **53,** 584 (1934).

[303] Federal Phosphorus Co., BP 370,774.



(II) (III) (I)

ALDEHYDES AND KETONES

Benzaldehyde (m.p. −13.5°, b.p. 179°) is used largely in perfumery, and is an intermediate for the important triphenylmethane dye Malachite Green. Substituted benzaldehydes are useful intermediates for some other dyes of the triphenylmethane series. When a mixture of benzal chloride and benzotrichloride is hydrolyzed by iron powder and boiling water or by dilute sulfuric acid at about 60°, benzaldehyde and benzoic acid are obtained ($PhCHCl_2 + H_2O \longrightarrow PhCHO + 2HCl$; $PhCCl_3 + 2H_2O \longrightarrow PhCOOH + 3HCl$). The oily aldehyde is separated, washed with sodium carbonate solution, and purified by distillation. Oxidation of toluene with manganese dioxide and sulfuric acid gives benzaldehyde free from chloro compounds. Toluene can be oxidized catalytically to benzaldehyde in the vapor phase by means of oxygen, diphenyl being used as a heat-transfer agent.[307] The *m*-dialkylbenzenes react readily with carbon monoxide and hydrochloric acid, the mixture functioning as formyl chloride, to yield the aldehyde, and benzaldehyde can also be synthesized from benzene and carbon monoxide in presence of aluminium chloride at a high pressure.[308] Small amounts of anthracene and triphenylmethane may be formed simultaneously.[309] The Cannizzaro reaction on benzaldehyde ($2PhCHO + KOH \longrightarrow PhCOOK + PhCH_2OH$) gives benzyl alcohol (b.p. 205.4°), which is a useful solvent and also has antiseptic and local anaesthetic properties. Several of its esters (e.g., benzyl succinate and fumarate) have medicinal value. Benzoyl chloride can be prepared by the action of chlorine on benzaldehyde ($PhCHO + Cl_2 \longrightarrow PhCOCl + HCl$),[310] and the method can be used as a procedure for the preparation of *o*-chlorobenzoyl chloride from *o*-chlorobenzaldehyde.[311]

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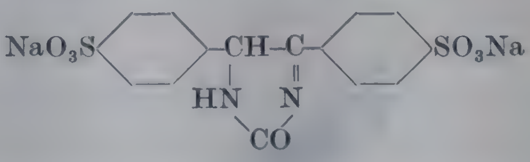
[304] Swann Research Corp., USP 1,891,543; IG, BP 409,615; Finzi and Bellavito, *Gazz. chim. ital.* **64**, 335 (1934); IG, BP 390,556; 290,029 ; Popkin, USP 2,448,823 ; Ciba, SP 233,185 ; 234,944–8.

[305] IG, BP 358,056.

[306] IG, BP 381,212.

[307] Reynolds, USP 2,081,120.

o- and *p*-Chlorobenzaldehydes (*o*-, b.p. 208°/748 mm.; *p*-, m.p. 47.5°) are prepared from the corresponding benzal chlorides[64, 312] or by direct oxidation of the chlorotoluenes. *m*-Chlorobenzaldehyde (m.p. 17–18°; b.p. 84–86°/8 mm.), which oxidizes readily on exposure to air, is obtained by reduction of *m*-nitrobenzaldehyde to *m*-aminobenzaldehyde with stannous chloride and hydrochloric acid; the amino group is then replaced by chlorine by the Sandmeyer reaction.[313] 2,5-Dichlorobenzaldehyde (m.p. 58°) is the main product of the chlorination of benzaldehyde with iodine or antimony as carrier. The more important intermediate, 2,6-dichlorobenzaldehyde (m.p. 71°), is prepared from 2,6-dichlorotoluene by oxidation with manganese dioxide and sulfuric acid.[314] Benzaldehyde-*o*-sulfonic acid and -2,4-disulfonic acid are important intermediates for the preparation of acid triphenylmethane dyes. The former can be prepared by heating *o*-chlorobenzaldehyde with aqueous sodium carbonate and bisulfite under pressure at about 200° or by the oxidation of toluene-*o*-sulfonic acid. The 2,4-disulfonic acid is prepared by the oxidation of toluene-2,4-disulfonic acid by manganous sulfate, potassium permanganate, and sulfuric acid.[315] An interesting use for benzaldehyde-*p*-sulfonic acid is the production of the imidazolone (Blankophor W, Ultrasan, I.G.), claimed



Blankophor W

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[308] See for instance du Pont, BP 445,300; 445,554; Holloway and Krase, *Ind. Eng. Chem.* **25,** 497 (1933).

[309] Hey, *JCS* 72 (**1935**).

[310] Wohler and Liebig, *Ann.* **3,** 262 (1832).

[311] Clarke and Taylor, *OSCV* I, p. 155.

[312] Erdmann and Kirchhoff (1888); McEwen, *OSCV* II, p. 133.

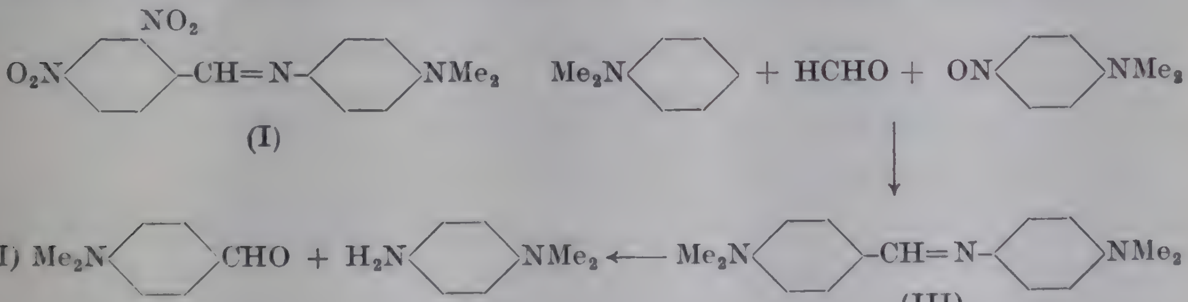
[64] See p. 65.

[313] MLB, DRP 31,842; Buck and Ide, *OSCV* II, p. 130.

[314] Geigy, DRP 199,943; see also Lock, *Ber.* **72,** 303 (1939).

[315] *BIOS* 959.

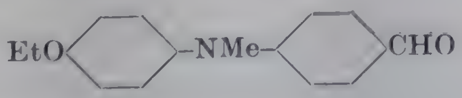
to protect wool and silk against the action of light. Nitration of benzaldehyde, best effected by potassium nitrate in concentrated sulfuric acid below 10°, gives *m*-nitrobenzaldehyde (65%) and the *o*-compound (20%); on pouring into water and pressing the pasty mass, *m*-nitrobenzaldehyde (yellow needles, m.p. 58°) is obtained as a solid. The *o*-compound is converted into indigo by treatment with acetone and alkali. *p*-Nitrobenzaldehyde (m.p. 106°) and 2,4-dinitrobenzaldehyde (m.p. 72°) are best prepared from the corresponding nitrotoluenes. Oxidation of *p*-nitrotoluene with chromic acid in glacial acetic acid and acetic anhydride gives *p*-nitrobenzaldiacetate, which is then hydrolyzed by dilute sulfuric acid.[316] Condensation of 2,4-dinitrotoluene with *p*-nitrosodimethylaniline in boiling alcohol gives the anil (I), hydrolyzed to 2,4-dinitrobenzaldehyde by boiling aqueous hydrochloric acid.[317] *p*-Dimethylaminobenzaldehyde (II), Ehrlich's reagent for the indole nucleus in tryptophane, is conveniently prepared by direct formylation of dimethylaniline with N-methylformanilide ($PhNMe_2 + PhNMeCHO \xrightarrow{POCl_3} Me_2N\text{-}C_6H_4CHO + PhNHMe$). It can also be prepared[318] in nearly quantitative yield by heating a mixture of dimethylaniline, 40% formalin, and *p*-nitrosodimethylaniline hydrochloride and 28% sulfuric acid at 90° for 2 hours; the first stage of the reaction is probably the formation of the anil (III), which then undergoes hydrolysis to (II) and *p*-aminodimethylaniline. *N*-*p*-Ethoxyphenyl-*N*-methyl-*p*-aminobenzaldehyde (IV) is prepared[10] in 92% yield when 4-ethoxy-*N*-methyldiphenylamine is treated in *o*-dichlorobenzene solution at 25° with *N*-methylformanilide and phosphorus oxychloride during 24 hours.

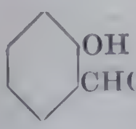

(I)

(II)

(III)

Salicylaldehyde (V; b.p. 197°) and the largely used aromatic coumarin (m.p. 70°) provide an important outlet for *o*-cresol. Salicylaldehyde can be prepared by oxidation of the benzenesulfonyl or *p*-toluenesulfonyl ester

(IV) 

 (V)

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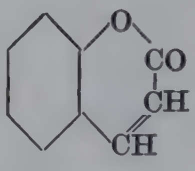
[316] Lieberman and Connor, *OSCV* II, p. 441.

[317] Bennett and Bell, *ibid.* p. 223.

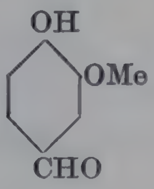
[318] See also Adams and Coleman, *ibid.* I, p. 214.

[10] See p. 50.

of *o*-cresol with manganese dioxide and 70–80% sulfuric acid at 95° and subsequent alkaline hydrolysis. Coumarin can then be prepared from salicylaldehyde by the Perkin condensation with acetic anhydride and sodium acetate. Another process[319] for the manufacture of coumarin from *o*-cresol is to protect the hydroxyl group as the carbonate by means of phosgene, dichlorinate the methyl group by chlorination at 170°, and condense with potassium acetate at 200–225°. *m*-Hydroxybenzaldehyde (m.p. 108°), an intermediate for the Patent Blues, is made from the nitro compound by reduction, diazotization, and hydrolysis.[320] Vanillin (VI; m.p. 80–81°), an important flavoring agent, is prepared synthetically from guaiacol.[319]

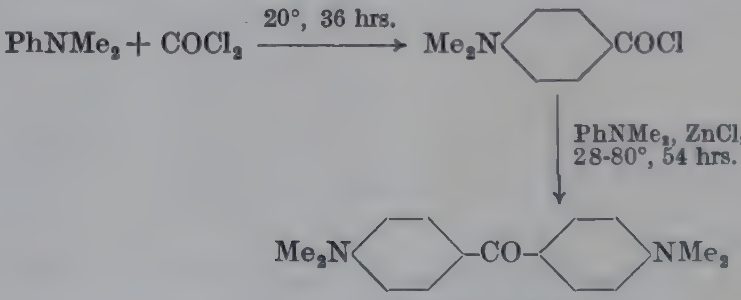


Coumarin

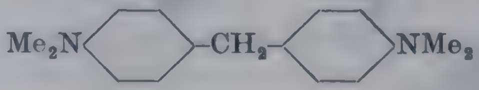


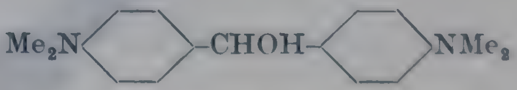
(VI)

Tetramethyldiaminobenzophenone (Michler's ketone) and the tetraethyl analog ("ethyl ketone") are important intermediates for triphenylmethane dyes. They are prepared[6] by condensation of the dialkylaniline (4 moles) with phosgene (1 mole). The dialkylaniline is used in excess to act as an acid-binding agent, and is recovered at the end of the reaction by treatment with warm dilute hydrochloric acid, which does not dissolve the less basic ketone (76% yield calculated on the amine consumed). Michler's ketone crystallizes from xylene in colorless plates, m.p. 175°. Tetramethyldiaminodiphenylmethane (VII) and the benzhydrol (VIII), which can be obtained by reduction of Michler's ketone, are largely used intermediates for Auramine and for triphenylmethane dyes, and they are prepared from



Michler's ketone

(VII)




(VIII)

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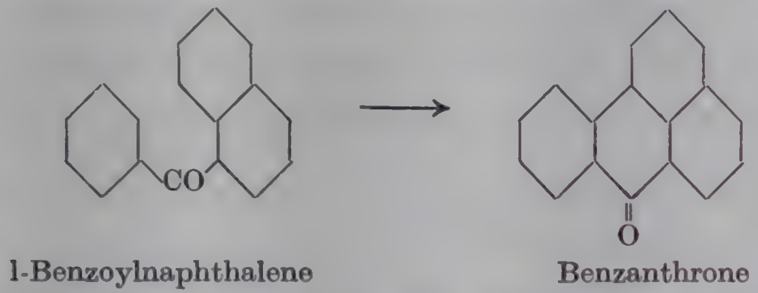
[319] *BIOS* 665.

[320] Tiemann and Ludwig, *Ber.* **15**, 2045 (1882); Woodward, *Org. Syntheses* **25**, 55 (1945).

[6] See p. 50.

dimethylaniline; condensation with formaldehyde in presence of sulfuric acid gives (VII), which is dissolved in dilute acetic and hydrochloric acids and oxidized by lead peroxide at 0° to (VIII).

Phenyl α-naphthyl ketones are of interest on account of their convertibility into benzanthrone and its derivatives by the action of aluminium chloride.[321] Thus benzanthrone itself is formed from 1-benzoylnaphthalene;



and dibenzpyrenequinones,[322] which are valuable vat dyes, are prepared from 1,4- and 1,5-dibenzoylnaphthalene. 1-Benzoylnaphthalene (m.p. 75.5°) can be prepared by the Friedel-Crafts reaction either between benzoyl chloride and naphthalene, when about 20% of the β-isomer is simultaneously formed, or between α-naphthoyl chloride and benzene. Phenyl 4-hydroxy-1-naphthyl ketone has been suggested as a coupling component for azoic dyes.[129] 1,5-Dibenzoylnaphthalene (m.p. 186.5°) is the main product of the interaction of 1-benzoylnaphthalene with a second mole of benzoyl chloride in presence of aluminium chloride; the 1,8-compound is a by-product.[323] 1,4-Dibenzoylnaphthalene (m.p. 106°) can be prepared by the nitric acid oxidation of 1-benzoyl-4-benzylnaphthalene obtained by a Friedel-Crafts reaction between benzoyl chloride and 1-benzylnaphthalene;[324] the latter (m.p. 59°) is the main product when naphthalene is condensed with benzyl chloride and a little aluminium chloride at 80–90°, higher temperatures leading to the β-compound.

CARBOXYLIC ACIDS

Although there are many methods available for the introduction of carboxyl groups into aromatic compounds, the few technically important acids are made mainly by oxidation of a side chain and, in the case of phenolic acids, by the Kolbe-Schmitt reaction, in which the sodium phenolate is heated with carbon dioxide under pressure. Benzoic acid free from nuclear chlorine can be obtained in 55–58% yield, together with benzophenone as the main by-product, by condensation of benzene with phosgene in presence of aluminium chloride, with liquid phosgene as solvent.[325] Carboxylic acids of polycyclic compounds containing not less than four fused rings can be prepared in good yield by the action of phosgene, fused alkali or alkaline earth, and aluminium chloride. Thus the metal phthalocyanines yield tetracarboxylic acids; benzanthrone, indigo, dibenzopyrenequinone, and pyranthrone yield dicarboxylic acids; anthanthrone, 3-bromobenzanthrone, 3,3′-dibenzanthronylsulfide, 3,9-dibromobenzanthrone, isoviolanthrone, and 7,8-phthaloylacridone yield only monocarboxylic acids.[326] The carbonation of Grignard compounds is a useful laboratory method for the introduction of a carboxyl group, and the carbonation of the lithium derivative of 3-bromopyridine appears to be a technically feasible route to nicotinic acid (pyridine-3-carboxylic acid).[327] α-Naphthoic acid is conveniently prepared by carbonation of α-naphthylmagnesium bromide,[328] and β-naphthoic acid by the hypochlorite oxidation of 2-acetylnaphthalene ($ArCOCH_3 + 3NaOCl \longrightarrow ArCOONa + CHCl_3 + 2NaOH$).[329]

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[321] Scholl and Seer, *Ann.* **394,** 111 (1912). For the preparation of α-naphthyl ketones free from the β-isomers, see Baddeley, BP 591,610; USP 2,487,777.

[322] See Chapter XXXII.

[129] See p. 83.

[323] IG, BP 279,506.

[324] IG, BP 333,666.

Benzoic acid occurs naturally in gum benzoin and can be isolated from coal tar.[81] Several methods of manufacture based on toluene are used. One is hydrolysis of benzotrichloride, mentioned earlier in connection with benzaldehyde. A procedure by which pure benzoic acid (m.p. 122°) is obtained from benzotrichloride involves partial hydrolysis with exactly one mole of water at about 100° and distillation of the benzoyl chloride (b.p. 197°) formed ($PhCCl_3 + H_2O \longrightarrow PhCOCl + 2HCl$). Further hydrolysis with excess water gives pure benzoic acid. The acid chloride is a reagent for benzoylation, e.g., of J-acid and the aminoanthraquinones. The direct oxidation of toluene gives benzoic acid free from chloro compounds, but it is difficult to obtain good yields. Among oxidizing agents that have been used are manganese dioxide and sulfuric acid, aqueous sodium dichromate and benzoic acid at 320° and 200 atm. pressure, and air at 130–135° in presence of cobalt naphthenate as catalyst.[330, 331] An excellent method for the production of chlorine-free benzoic acid is decarboxylation of phthalic acid by passing the vapors leaving a phthalic anhydride converter over a catalyst of zinc and aluminium oxides on pumice at 340°. The yield is about 90%, and the benzoic acid, which contains a little phthalic acid and α-naphthoquinone, is purified by treatment with sodium bisulfite solution which dissolves the two impurities.[332, 333] Autoclaving in an aqueous medium at 200–250° for a few hours decarboxylates phthalic acid and anhydride to benzoic acid.[334] It has also been mentioned that benzoic acid can be obtained in 78% yield by catalytic oxidation of naphthalene with a " benzoic acid catalyst "[6] and in 31% yield with stannous vanadate as catalyst and a temperature of 300°.[335] Benzoic acid is an intermediate for some chrome colors and is used as a catalyst for the phenylation of Rosaniline; it has pharmaceutical uses as a mild antiseptic; the sodium salt is a widely used preservative for foods. For pharmaceutical and food purposes it can be purified by sublimation. Esters of benzoic acid (e.g., benzyl, guaiacol, and β-naphthyl benzoates) have useful medicinal properties; benzyl benzoate is a plasticizer for cellulose nitrate. *o*- and *p*-Chlorobenzoic and 2,4-dichlorobenzoic acids (m.p. 142, 243°, 164°) are prepared from the corresponding benzotrichlorides by hydrolysis or from the chlorotoluenes by oxidation either with boiling 8–9% permanganate solution[336] or with 34% sodium dichromate solution at 280–290° and 200 atm. pressure.[6, 64] 2,4-Dichlorobenzoic acid, besides being a dye intermediate, is useful for the synthesis of the antimalarial drug Atabrine. 2,5-Dichlorobenzoyl chloride is obtained in 93% yield[10] by the condensation of *p*-dichlorobenzene in tetrachloroethane solution with phosgene in presence of aluminium chloride at 30–50°. The by-product, recovered as the residue when the chloride is purified by vacuum distillation, is 2,5,2′,5′-tetrachlorobenzophenone.

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[325] Rueggeberg, Frantz, and Ginsburg, *Ind. Eng. Chem.* **38,** 624 (1946); see also Hayashi, *J. Soc. Chem. Ind. Japan* **47,** 536 (1944).

[326] IG, BP 510,901.

[327] Gilman and Spatz, *JACS* **62,** 446 (1940).

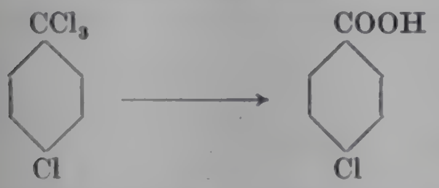
[328] Acree (1904); Gilman, St. John, and Schulze, *OSCV* II, p. 425.

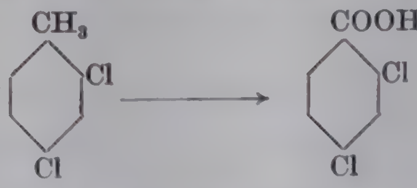
[329] Newman and Holmes, *ibid.*, p. 428; for a discussion of various methods for preparing the naphthoic acids, see Wahl *et al.*, *Bull. soc. chim. France* (5) **6,** 533 (1939).

[81] See p. 70.

[330] *BIOS* **666.**

[331] *BIOS* **1786.**





Oxidation of *p*-nitrotoluene with sodium dichromate and 50% sulfuric acid at the boil gives *p*-nitrobenzoic acid (m.p. 238°) in 85% yield.[337] It is obtained technically in 94% yield by adding 76% sodium dichromate solution (9 parts) and a solution of *p*-nitrotoluene (3.2 parts) in 96% sulfuric acid (9.4 parts) to 52% sulfuric acid (6.5 parts) at 70°. The mixture is agitated at 80° for 4 hours and run into water, when the nitrobenzoic acid precipitates. *p*-Aminobenzoic acid (m.p. 187°), obtained in 97% yield by

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[332] *CIOS* Item No. 22, File XXVII–85.

[333] Among numerous patents on this technically important decarboxylation, a few are: Selden Co., USP 1,956,718; 1,961,150; 1,966,067; du Pont, USP 1,962,175.

[334] Sultanov, RP 66,248.

[6] See p. 50.

[335] Sasayama, *J. Soc. Chem. Ind. Japan* **46**, 1225 (1943).

[336] Emmerling (1875); Clarke and Taylor, *OSCV* II, p. 135.

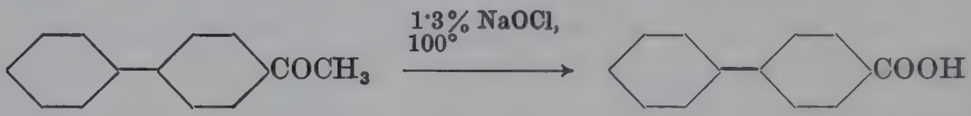
[64] See p. 65.

[10] See p. 50.

[337] Kamm and Matthews, *ibid.* I, p. 392.

reduction of *p*-nitrobenzoic acid with iron and hydrochloric acid, has exceedingly interesting and complex physiological properties which are being actively investigated. Ethyl *p*-aminobenzoate is a cheap local anaesthetic (benzocaine), prepared by reduction of ethyl *p*-nitrobenzoate, e.g., by iron and acid or by hydrogen in presence of platinum oxide catalyst.[338] A good laboratory method for the preparation of *m*-nitrobenzoic acid is to saponify methyl *m*-nitrobenzoate obtained by nitration of methyl benzoate.[339] 3,5-Dinitrobenzoic acid (m.p. 204–205°), obtained by dinitration of benzoic acid, is a useful reagent for the characterization of alcohols, which give solid, readily crystallizable esters when warmed with the acid chloride. 2-Chloro-5-aminobenzoic acid (m.p. 188°) is obtained by nitration and reduction of *o*-chlorobenzoic acid. Nitration of *p*-chlorobenzoic acid with mixed acid at 105° gives 4-chloro-3,5-dinitrobenzoic acid in 90% yield.

Diphenyl-4-carboxylic acid (m.p. 228°) is prepared by an interesting method. Diphenyl is condensed with acetyl chloride and aluminium chloride in nitrobenzene solution at 30° to form 4-acetodiphenyl, which is oxidized to the carboxylic acid by sodium hypochlorite.



Phthalic anhydride is an outstandingly important intermediate for dyes (indigo, phthaleins, anthraquinones, phthalocyanines), resins, and plasticizers; its annual production is over 120 million pounds. The United States production of anthraquinone dyes was over 5 million pounds in 1942. The original process of manufacture from naphthalene by oxidation with fuming sulfuric acid in presence of mercury has now been replaced by air oxidation with vanadium pentoxide on a suitable carrier such as silica and in presence of promoters such as potassium sulfate (Gibbs, 1918).[4, 126, 332, 340–344] The reaction is highly exothermic at about 350°; 5,460 B.t.u. per lb. of naphthalene is the heat of oxidation to phthalic anhydride, and the unavoidable complete combustion of part of the material raises the heat liberated to about 10,000 B.t.u.; hence the essential problem in the process is dissipation of this heat while the catalyst is maintained at the optimum temperature. The usual catalytic converter consists of a large number of steel tubes, each about one inch diameter and 3–10 feet in length, packed into a steel shell which functions as a heat exchanger. The tubes are surrounded by mercury or by a molten salt (e.g., potassium nitrate), and the heat exchange is effected by the vaporization and condensation of the mercury or by the circulation of the fused salt by means of a pump and removal of the heat of reaction before the salt returns to the converter bath. Air, preheated to 160° by heat exchange with the converter exit gases, is led into molten naphthalene (m.p. 78.8–79.5°), and the naphthalene-air mixture enters the converter at the top and passes downward through the catalyst. The gases leaving the converter at the bottom are cooled to 160° in the air preheater, and the crude phthalic anhydride, containing α-naphthoquinone and maleic anhydride which are by-products representing earlier and later stages of the oxidation, is collected in a series of condensing chambers. Separation of the product in different grades is possible at this stage, and final purification is effected by treatment with a small amount of sulfuric acid at 200°, neutralization with calcium carbonate, and vacuum distillation. The yield is about 80% of theory. Phthalic anhydride sublimes in long colorless needles, m.p. 132°. The physical form of the phthalic anhydride is important technically, and patents for preparing it in flakes,[345] shot-like pellets, or comminuted crystals[346] have been taken.

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[338] Adams and Cohen, *ibid.* p. 240.

[339] Kamm and Segur, *ibid.* pp. 373, 391.

[4] See p. 50.

[126] See p. 82.

[332] See p. 139.

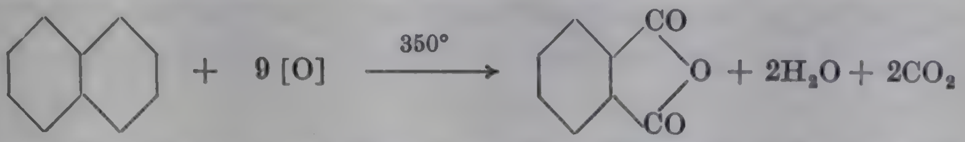
[340] Marek and Hahn, Catalytic Oxidation of Organic Compounds in the Vapor Phase, Reinhold, New York, 1932.

[341] *BIOS* 753.

[342] *BIOS* 875.

[343] *BIOS* 935.

[344] The oxidation of naphthalene to phthalic anhydride in the combustion chamber of a Diesel type engine has been claimed by Chebotar and Wallach, USP 2,084,382.



An important development in recent years is the production of phthalic anhydride from *o*-xylene which is becoming available in the United States from petroleum sources.[347] A process, with details of plant, for the manufacture of phthalic anhydride by the oxidation of *o*-xylene has been described.[348] In one method of converting *o*-xylene into phthalic anhydride a mixture of the hydrocarbon and steam is passed over Raney nickel at about 500° for a period not exceeding two seconds.[349]

Esters of phthalic acid are largely used plasticizers. Dimethyl phthalate finds extensive use in mosquito repellants.

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[345] National Aniline Co., USP 1,817,304.

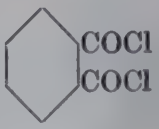
[346] Selden Co., USP 1,837,869; 1,789,967.

[347] See for instance Allied Chemical and Dyestuff, USP 2,332,370.

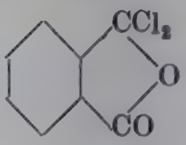
[348] Levine, *Trans. Am. Inst. Chem. Engrs.* 168 (1947).

[349] Rolleston, USP 2,416,350; see also Allied Chemical and Dyestuff, USP 2,329,638; Parks and Allard, *Ind. Eng. Chem.* **31**, 1162 (1939); Welty and Rollman, USP 2,485,342; 2,489,346-7.

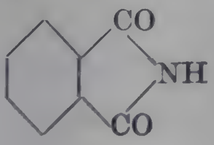
On heating phthalic anhydride with phosphorus pentachloride at 150° and distilling the product, the normal acid chloride (I; m.p. 16°, b.p. 281°) is obtained,[350] and this rearranges to *as*-phthalyl chloride (II; m.p. 89°) on prolonged treatment with aluminium chloride at 95° The action of ammonia on phthalic anhydride leads to phthalimide (III; m.p. 234°),



(I)



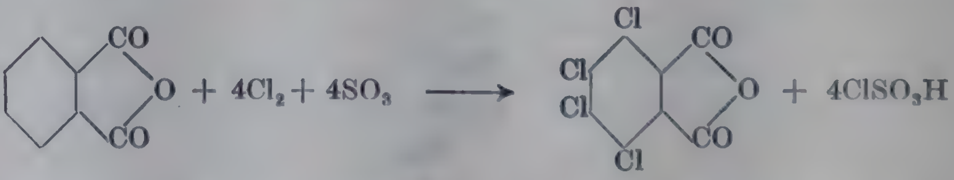
(II)



(III)

which is acid in character and forms a potassium salt, used in the Gabriel synthesis of primary amines. Suitable conditions for the preparation of (III) are the high-pressure reaction of the anhydrous reactants at about 250° and the fusion of phthalic anhydride with 28% aqueous ammonia or with ammonium carbonate at 300° (nearly quantitative yield).[351]

Dichloro- and tetrachlorophthalic anhydrides are used in making phthalein dyes. The tetrachloro compound is especially useful and it has other possibilities as an intermediate.[352] The chlorinations can be carried out in oleum with iodine as carrier. At low temperature the product is mainly 3,6-dichlorophthalic anhydride, m.p. 190°, together with the 3,4- and 4,5-compounds. The 3,4-, 3,6-, and 4,5-dichlorophthalic acids can be separated by a method[353] depending on the fact that the different isomers require different concentrations of sulfuric acid for conversion into the anhydride. Chlorination of phthalic acid in oleum gives a mixture of isomers containing only 20% of 4,5-dichlorophthalic acid, whereas chlorination in aqueous solution gives this acid in 65% yield.[7] Further chlorination takes place with 60% oleum and at the higher temperature of 200°. The chlorosulfonic acid formed is distilled; on cooling and adding to ice, tetrachlorophthalic anhydride, m.p. 255°, is obtained. 4-Bromophthalic acid (m.p. 173–175°) can be prepared by bromination of phthalic acid in aqueous solution, and is " the best and cheapest available halogeno phthalic acid."[7] Tetraiodophthalic anhydride (m.p. 327–328°) is obtained[354] by



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[350] Ott, *OSCV* II, p. 528.

[351] Noyes and Porter, *ibid.* I, p. 457.

[352] Lawlor, *Ind. Eng. Chem.* **39**, 1424 (1947).

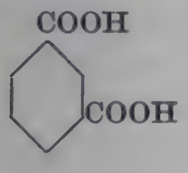
[353] ICI, BP 396,735.

[7] See p. 50.

[354] Allen, Cressman, and Johnson, *Org. Syntheses* **27**, 78 (1947).

iodination in 60% oleum at 45–175°. Nitration of phthalic anhydride in sulfuric acid with fuming nitric acid (sp. gr. 1.51) at 100–110° gives a mixture of about equal parts of 3- and 4-nitrophthalic acids (m.p. 218° and 165° respectively), which can be separated by fractional crystallization from water[355] or by fractional distillation of the esters.[356] 4-Nitrophthalic acid is best prepared by nitration of phthalimide, which gives a 52–53% yield of 4-nitrophthalimide (m.p. 198°), and hydrolysis of the latter with aqueous caustic soda.[357]

Isophthalic acid (IV; m.p. 345–347°) and terephthalic acid (V; sublimes without melting at 300°) can be prepared from the corresponding xylenes by complete chlorination of the side chains, followed by hydrolysis. These acids are mainly used as the chlorides (e.g., VI; m.p. 83–84°), which can be prepared directly from the corresponding xylenehexachloride. Thus (VI) is obtained in quantitative yield by treating *p*-xylenehexachloride (6 kg.) with sublimed ferric chloride (0.5 g.), adding at 135–140° during 8 hours a solution of ferric chloride (0.5 g.) in water (550 cc.) and heating further at 140° for a few hours.[8] Terephthalic acid can also be made from *p*-cymene, which occurs naturally in spruce turpentine and which can also be produced by dehydrogenation of several terpenes.[358] The best procedure would appear to be to oxidize *p*-cymene in the vapor phase with air in presence of vanadium pentoxide to *p*-toluic acid[359] with subsequent oxidation of the latter to terephthalic acid, e.g., with permanganate.[360] The preparation of terephthalic acid from toluene via *p*-methylacetophenone,[361] the latter being oxidized successively by nitric acid and by alkaline permanganate, has also been described.[362]



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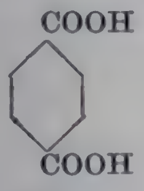

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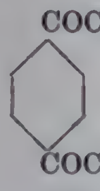
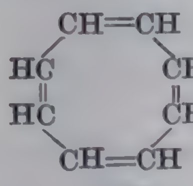


(VI)



(VII)

A remarkable reaction of acetylene is its polymerization, in tetrahydrofuran solution and in presence of nickel cyanide catalyst, to cyclooctatetraene (VII). The chemistry of this substance has been extensively investigated, and a possible technical application is its oxidation by means of hypochlorite or chromic acid to terephthalaldehyde and terephthalic acid.[363, 364]

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[355] Culhane and Woodward, *OSCV* I, 408.

[356] Bogert and Boroschek, *JACS* **23,** 743 (1901).

[357] Levy and Stephen, *JCS*. 79 (**1931**); Huntress *et al.*, *OSCV* II, pp. 457, 459.

[8] See p. 50.

[358] See *e.g.*, Joshi *et al.*, *Current Sci.* (*India*) **17,** 359 (1948).

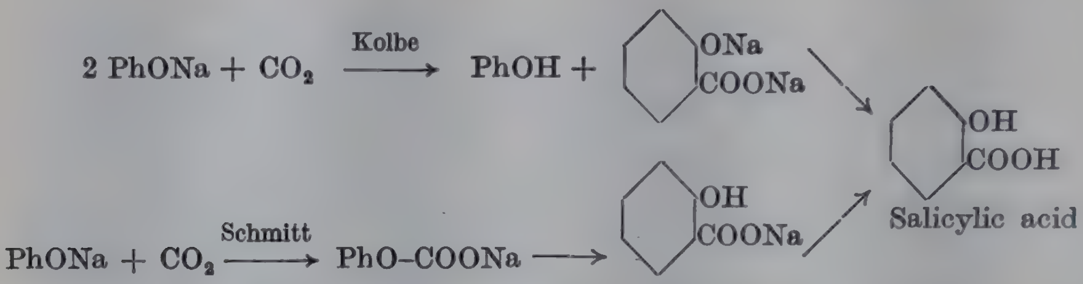
[359] Senseman and Stubbs, *Ind. Eng. Chem.* **23,** 1129 (1931); see also Tuley and Marvel, *Org. Syntheses* **27,** 86 (1941).

[360] See also Bogert and Harris, *JACS* **41,** 1680 (1919). For the air oxidation of *p*-xylene to terephthalic acid, see ICI, BP 623,836.

[361] Adams and Noller, *OSCV* I, p. 109.

[362] Koelsch, *Org. Syntheses* **26,** 95 (1946).

Salicylic acid (colorless needles, m.p. 159°) is manufactured[365, 223] by the Schmitt modification of the Kolbe reaction.[365a] Pure phenol (m.p. 40.6°) is dissolved in 40% caustic soda solution (1% excess of one mole of NaOH) in a closed mixer. The solution is charged into the main reactor, which is a nickel-steel autoclave, equipped with baffles and an efficient agitator, suitable heating device for raising the temperature of the reaction mixture uniformly to about 200°, inlet for carbon dioxide, and vacuum connection. At a temperature of 180° and a pressure of 20–30 mm., all the water is evaporated, and after cooling to 150°, carbon dioxide (free from air) is led in. A pressure of 4–5 atm. and a temperature of 150–160° are maintained for 36 hours, the heat liberated during the carbonation being removed by circulating water in the jacket. The temperature is finally raised to 180° and, when no more carbon dioxide is absorbed, the reaction is complete. The sodium salicylate is taken up in water, the solution clarified by decolorizing carbon, salicylic acid is precipitated by means of sulfuric acid and purified by sublimation at 150° and 15 mm. pressure (overall yield 90–92% based on phenol). Salicylic acid is an intermediate for mordant azo dyes, and an important medicinal chemical used as the sodium salt, the acetate (aspirin) and other derivatives. The annual production is over 15 million pounds.



When the Kolbe reaction is carried out on potassium phenolate at a temperature of 200–220°, *p*-hydroxybenzoic acid is obtained in 85% yield.[6] This acid, which can also be prepared[366] by heating potassium salicylate at 230°, is useful as a food preservative, especially in the form of its ethyl and propyl esters; the esters have antiseptic and anaesthetic properties. Methylation of *p*-hydroxybenzoic acid with dimethyl sulfate and alkali in

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[363] *BIOS* **352.** [364] *BIOS* **137.** [365] *FIAT* **744.**

[223] See p. 111.

[365a] For a recent study of the Kolbe-Schmitt reaction, see Cameron *et al.*, *J. Org. Chem.* **15,** 233 (1950).

[6] See p. 50.

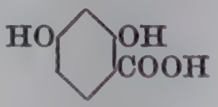
[366] Buehler and Cate, *OSCV* II, p. 341.

the usual manner gives anisic acid (m.p. 184°), which on nitration in 96% sulfuric acid with a dilute mixed acid gives 3-nitro-4-methoxybenzoic acid (m.p. 195–196°).

β-Resorcylic acid (VIII; m.p. 213), readily obtainable[367] by treating resorcinol with carbon dioxide in boiling potassium bicarbonate solution, has been occasionally employed as a component for azo dyes; but it is in fact valueless since it is partly decarboxylated during coupling with diazonium salts. The ease with which it loses carbon dioxide to form resorcinol, e.g., by being boiled with water, can be utilized for preparing 4-bromoresorcinol by bromination of (VIII) to the 5-bromo compound followed by decarboxylation.[368]

Benzene tri- and tetracarboxylic acids can be prepared by the controlled oxidation of bituminous coals with oxygen in presence of caustic soda at 200–300° under pressure.[369] Pyromellitic acid (benzene-1,2,4,5-tetracarboxylic acid; m.p. 262°) can be obtained in 6–8% yield by the oxidation of suitable charcoal either with sulfuric acid in presence of a little mercury[370] or with nitric acid.[371]

5-Hydroxytrimellitic acid (IX) is a new intermediate of considerable interest prepared from the coal-tar hydrocarbon pseudocumene.[10] Sulfonation with 95% sulfuric acid at 80° gives the sulfonic acid (X), which is oxidized to 5-sulfotrimellitic acid (XI) by alkaline permanganate at 80–90°. Alkali fusion then gives (IX). Chloro-pseudocumene provides another route.[371a] This acid has also been prepared by the carboxylation of crude xylene with an alkylphenylcarbamyl chloride in the presence of aluminium chloride; when the intermediate products are hydrolyzed and the mixture of the three xylic acids is sulfonated, oxidation gives only one sulfobenzenetricarboxylic acid, converted by alkali fusion into (IX).[372]



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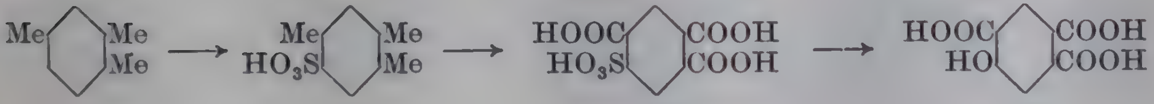

(X) (XI) (IX)

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[367] Bistrzycki and Kostanecki (1885); Nierenstein and Clibbens, *OSCV* II, p. 557.

[368] Zehenter (1881); Sandin and McKee, *OSCV* II, p. 100.

[369] France and Keibler, *Chem. Ind.* **58**, 580 (1946).

[370] Verneuil (1894); Philippi and Thelen, *OSCV* II, p. 551.

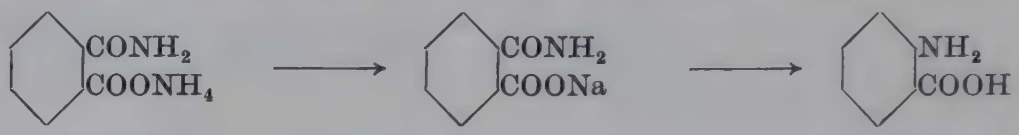
[371] Silberrad, DRP 214,252.

[10] See p. 50.

[371a] IG., BP 495,432.

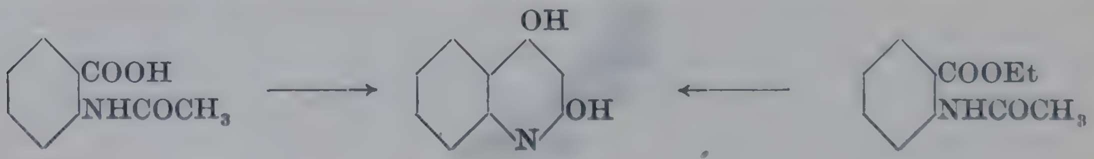
[372] ICI, BP 534,221.

Anthranilic acid (XII; colorless leaflets, m.p. 145°) was once produced in large quantities as an intermediate for indigo, but other starting materials are now used. The acid however is a useful intermediate for azo dyes, for thioindigo, and for a few anthraquinonoid vat dyes of the acridone type. Methyl anthranilate is a valuable perfume occurring naturally in jasmine and orange leaves. The manufacturing method[6] is an application of the Hofmann reaction to phthalamidic acid obtained as the ammonium salt (XIII) by treatment of phthalic anhydride with ammonia. Phthalic anhydride (6 parts) is added to 25% ammonia (corresponding to 1.4 parts of 100% ammonia) and water (8.5 parts), during which the temperature rises from 17° to 60°. After 30 hours more phthalic anhydride (6 parts) is added, followed immediately by 70% caustic soda solution (9.4 parts). The clear pale yellow solution is cooled to −2° and treated rapidly with sodium hypochlorite solution, prepared from 50% caustic soda solution (26 parts), water (37 parts), and chlorine (5.8 parts) and cooled to −8°. The temperature rises to 70° in about 10 minutes, and after being stirred for 45 minutes the solution is acidified to pH 6.5 with sulfuric acid with addition of some sodium bisulfite and decolorizing carbon. The mixture is filtered when at 53°, and the filtrate acidified with hydrochloric acid and sulfuric acid to pH 4. The precipitated anthranilic acid is filtered, washed, and dried (yield 88% from phthalic anhydride).



(XIII) (XII)

An interesting reaction[373] of *N*-acetylanthranilic acid (XIV) is its cyclization to 2,4-dihydroxyquinoline (XV) when heated with alkali above 150°; (XV), which is an azo dye intermediate, can also be prepared[374] by the action of sodium on ethyl *N*-acetylanthranilate (XVI), and of hydriodic acid and red phosphorus on diethyl *o*-nitrobenzoylmalonate.[375] 2,4-Dihydroxyquinoline is manufactured[10] as the monosodium derivative by fusion of (XIV) with caustic soda, caustic potash, and sodamide at 150–190° for a



(XIV) (XV) (XVI)

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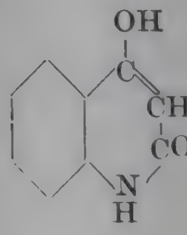
[6] See p. 50.
[373] BASF, DRP 117,167.
[374] Hoechst Farbw., DRP 102,894.
[375] Gabriel, *Ber.* **51**, 1507 (1918). See also Huntress and Bornstein, *JACS* **71**, 745 (1949).
[10] See p. 50.

few hours under conditions somewhat similar to those used for the indigo melt. The formation of the monosodium compound and other properties indicate that 2,4-dihydroxyquinoline exists chiefly as the cyclic amide



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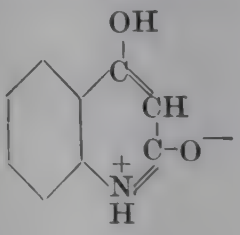
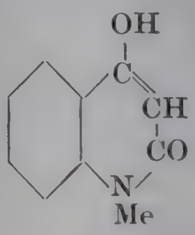
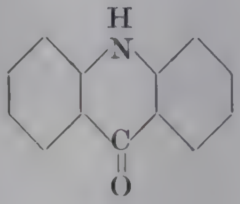


(XVIII)



(XIX)



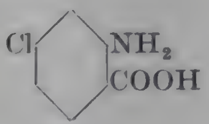
(XX)

(XVII) or as a resonance hybrid of the structures (XVII) and (XVIII). 4-Hydroxy-*N*-methyl-α-quinolone (XIX) is produced in one operation by refluxing *N*-methylanthranilic acid with acetic acid and anhydride for 12 hours.[10]

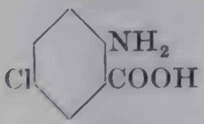
N-Phenylanthranilic acid (m.p. 184°), prepared by treatment of *o*-chlorobenzoic acid with boiling aniline in presence of potassium carbonate and copper oxide, is of interest on account of its ready cyclization when heated with concentrated sulfuric acid at 100° to acridone (XX; m.p. 354°).[376]

Oxidation of 4-chloro-acet-*o*-toluidide with potassium permanganate solution in presence of magnesium sulfate at about 95°, followed by deacetylation with 10% caustic soda solution at 100°, yields 4-chloroanthranilic acid (XXI; m.p. 240°), which can also be prepared by partial amination of 2,4-dichlorobenzoic acid. 5-Chloroanthranilic acid (XXII; m.p. 211–212°) is obtained by heating 2,5-dichlorobenzoic acid with ammonia under pressure or by treatment of anthranilic acid with sulfuryl chloride.[377]

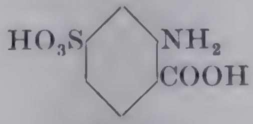
4-Sulfoanthranilic acid (XXIII), 5-sulfo-*N*-methylanthranilic acid (XXIV; R = Me), and the ethyl analog are useful for stabilizing diazonium salts in the form of the diazoamino compounds.[41] 4-Sulfoanthranilic acid is obtained[8] in 35% yield by heating *o*-nitrotoluene-4-sulfonic acid with 13% caustic soda solution at 100–103°. The *N*-alkyl compounds (XXIV) are prepared[8] from *o*-chlorobenzoic acid by heating with the alkylamine,



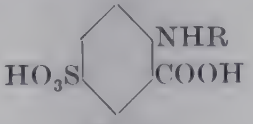
(XXI)



(XXII)



(XXIII)



(XXIV)

copper oxychloride, and aqueous caustic soda at 115° and sulfonating the *N*-alkylanthranilic acid.

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[10] See p. 50.

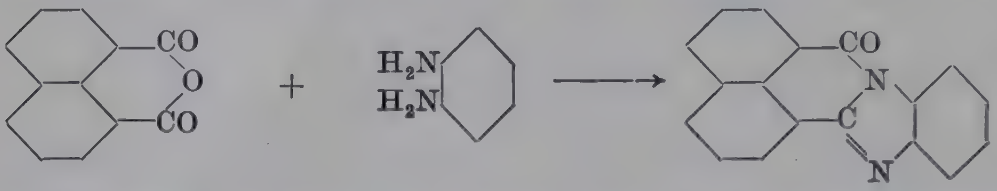
[376] Ullmann (1903); Allen and McKee, *OSCV* II, p. 15; Graebe and Lagodzinski (1892).

[377] See also Atkinson and Mitton, *JACS* **69**, 3142 (1947).

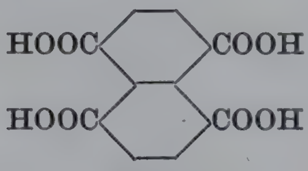
[41] See p. 57.

[8] See p. 50.

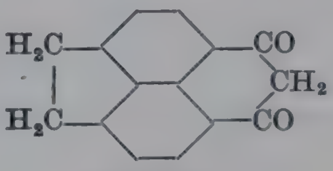
Naphthalic acid (naphthalene-1,8-dicarboxylic acid; needles, m.p. 270–271°),[378] obtained originally (Behr and von Dorp, 1874) by the oxidation of acenaphthene with chromic acid, can be prepared in 95% yield by oxidation of acenaphthenequinone suspended in caustic soda solution with hydrogen peroxide.[379] Like phthalic acid, it yields the anhydride (m.p. 274°) and the imide (m.p. 300°) very readily. Condensation of naphthalic anhydride with *o*-phenylenediamines leads to the imidazole derivative (XXV). When an *N*-alkylnaphthalimide is fused with alkali, two molecules condense in the unsubstituted *peri*-positions to form perylene derivatives which are useful vat dyes.[324] Naphthalene-1,4,5,8,-tetracarboxylic acid (XXVI) can be prepared by the oxidation of pyrenequinone or of the condensation product (XXVII) of malonyl chloride with acenaphthene or from naphthalene by a series of reactions involving dual condensation with malonyl chloride;[324] like naphthalic acid, it is an intermediate for the preparation of vat dyes.[322]



(XXV)

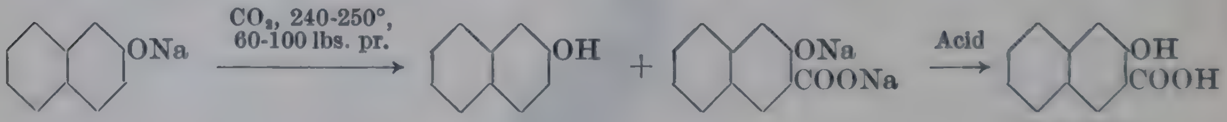


(XXVI)



(XXVII)

2-Hydroxy-3-naphthoic acid (XXVIII) is an important intermediate from which most of the azoic coupling components of the Naphtol AS type are derived.[129] United States production in 1942 was over a million pounds. Like salicylic acid, it is prepared by the action of carbon dioxide on dry sodium β-naphtholate. The yield depends on the employment of a specially designed autoclave and adherence to specific experimental conditions. The reactor can be a rotary autoclave containing iron balls or rails for grinding the reaction mass or a vertical autoclave provided with a powerful heavy-duty agitator and steam coils cast in the shell for heating with steam at 25 atm.



(XXVIII)

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[378] Leuck, Perkins and Whitmore, *JACS* **51**, 1831 (1929).

[379] Whiston, *J. Soc. Chem. Ind.* **43**, 370T (1924).

[324] See p. 137.

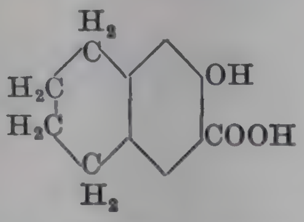
[322] See p. 137.

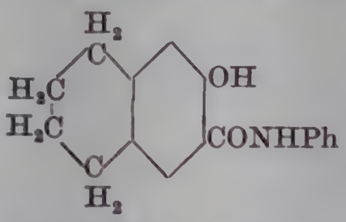
[129] See p. 83.

pressure. The IG use the second type of reactor and a process in which the carbonation is carried out in 3 stages with intermediate removal of the liberated β-naphthol by vacuum distillation.[6, 380, 381] The reaction product is finally dissolved in water, and neutralized to pH 6.8, when β-naphthol and tarry by-products separate. The clear filtrate is then acidified to Congo Red to precipitate the hydroxynaphthoic acid. Further purification is usually not necessary. 2-Hydroxy-3-naphthoic acid crystallizes in yellow scales, m.p. 216°.

The use of a diluent or solvent (e.g., dioxane, pyridine) in the above reaction has been suggested.[382] Zinc, magnesium and other salts of 2-hydroxy-3-naphthoic acid are luminescent.[383] Hexadecyl 2-hydroxy-3-naphthoate is a good water-proofing agent for cellulose fibers.[384] By heating sodium *ar*-tetrahydro-β-naphtholate with carbon dioxide at 160° under 10 atm. pressure (or 180° and 4–5 atm.), the carboxylic acid (XXIX; m.p. 180–182°) is obtained.[8, 385] The acid (XXIX) and its anilide (XXX) are also obtainable[386] by the treatment of 2-hydroxy-3-naphthoic acid and its anilide (Naphtol AS) with Raney nickel; (XXX) has been mentioned as a useful azoic coupling component.[129, 387] The ethyl ester of (XXIX) can be prepared in 94% yield by hydrogenation of ethyl 2-hydroxy-3-naphthoate in the presence of Raney nickel at 150° and 900 lbs. pressure.[388] 2-Amino-3-naphthoic acid (m.p. 216–217°) is a useful intermediate for the preparation of azo mordant dyes, and it is obtained in 70% yield by heating 2-hydroxy-3-naphthoic acid with 28% ammonia in presence of zinc chloride at 195° and 400 lbs. pressure for 36 hours.[389] 2,6-Dihydroxy-3-naphthoic acid may have some interest as an intermediate for the preparation of

(XXIX)





(XXX)

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[6] See p. 50.

[380] *BIOS* **1363.**

[381] Shorey, USP 1,450,990.

[382] Cone, USP 1,503,984; Calco, BP 511,393; USP 2,132,356–7; General Aniline and Film, USP 2,453,105.

[383] Burrell, Valk and Heyden Chemical Corp., USP 2,441,559.

[384] Oshima and Hayashi, *J. Soc. Chem. Ind. Japan* **44,** 821 (1941).

[8] See p. 50.

[385] Schroeter, *Ann.* **426,** 147 (1922); Robinson and Walker, *JCS* 1531 (**1935**).

[386] Shah, Tilak, and Venkataraman, *Proc. Indian Acad. Sci.* **28A,** 142 (1948).

[129] See p. 83.

[387] IG, BP 468,375.

[388] Arnold, Zaugg, and Sprung, *JACS* **63,** 1314 (1941).

[389] Allen and Bell, *Org. Syntheses* **22,** 19; Ciba, BP 250,598; Dutta, *Ber.* **67,** 1321 (1934).

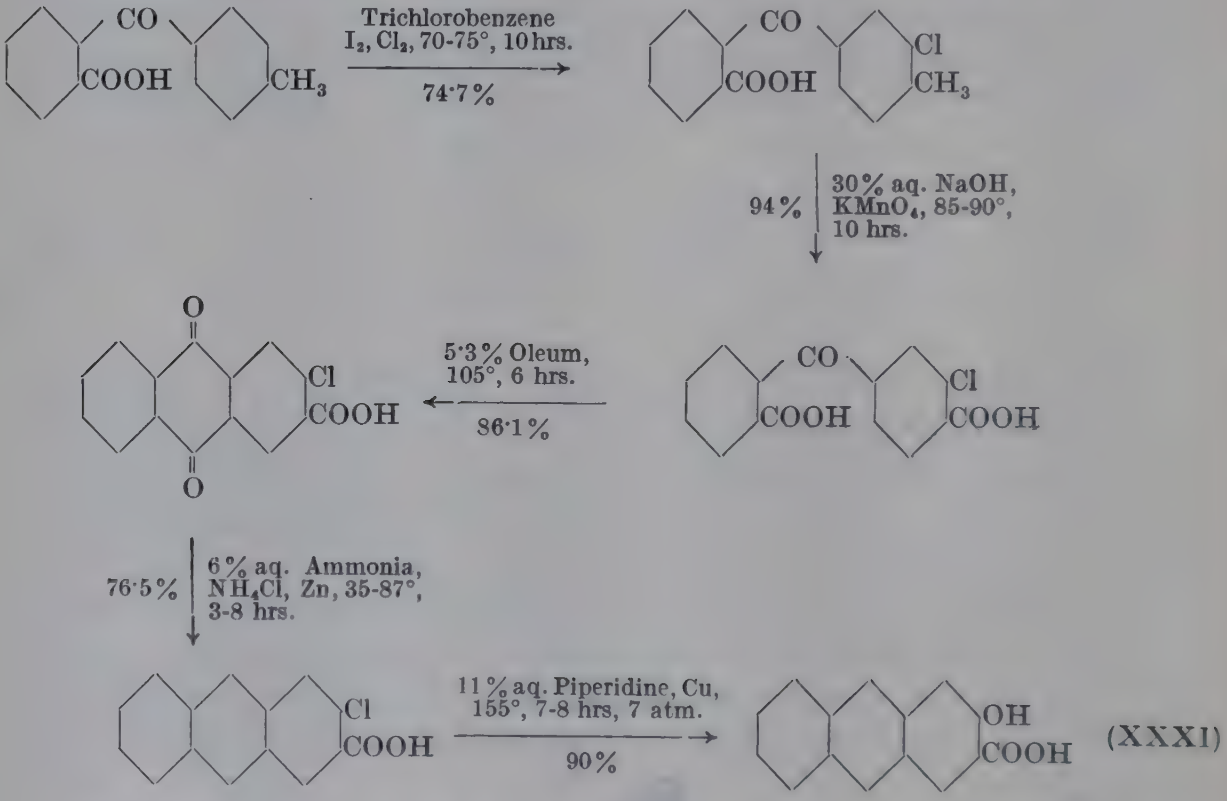
azoic coupling components. It is obtained by the alkali fusion of 2-hydroxy-6-sulfo-3-naphthoic acid, which results (together with the 8-sulfonic acid) from the sulfonation of 2-hydroxy-3-naphthoic acid.[390]

2-Hydroxy-1-naphthoic acid is formed by carrying out the Kolbe reaction at 120–145°; it isomerizes to the 3-acid on being heated at about 200° under pressure,[391] but the 1-acid also tends to decarboxylate very readily.

2-Hydroxyanthracene-3-carboxylic acid (XXXI) can be prepared[8] by the series of reactions in Chart 6 or by the Kolbe reaction on β-hydroxyanthracene.

CHART 6

PREPARATION OF 2-HYDROXYANTHRACENE-3-CARBOXYLIC ACID


CO
COOH
CH₃
Trichlorobenzene
I₂, Cl₂, 70-75°, 10 hrs.
74·7%
CO
COOH
Cl
CH₃
94%
30% aq. NaOH,
KMnO₄, 85-90°,
10 hrs.
O
O
Cl
COOH
5·3% Oleum,
105°, 6 hrs.
86·1%
CO
COOH
Cl
COOH
76·5%
6% aq. Ammonia,
NH₄Cl, Zn, 35-87°,
3-8 hrs.
Cl
COOH
11% aq. Piperidine, Cu,
155°, 7-8 hrs, 7 atm.
90%
OH
COOH
(XXXI)

Heterocyclic analogs of 2-hydroxy-3-naphthoic acid, used in making members of the Naphtol AS series, are prepared by similar applications of the Kolbe reaction to the appropriate phenols. Thus the dry sodium salt of 3-hydroxydibenzofuran (XXXII) heated with carbon dioxide at 265° (4–5 atm. pressure) for several hours gives the 2-carboxylic acid (XXXIII) in 84% yield. The method by which (XXXII) was first prepared will be mentioned later in connection with the constitution of Naphtol

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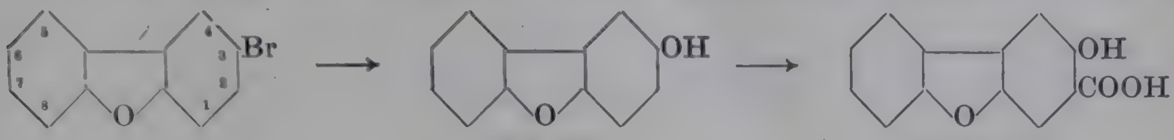
[390] Cross, *J. Soc. Dyers Colourists* **62**, 150 (1946).

[391] Schwenke, USP 1,700,546.

[8] See p. 50.

AS-S;[129] the method now preferred is the bromination of dibenzofuran, isolated from coal tar, in boiling carbon tetrachloride and hydrolysis of

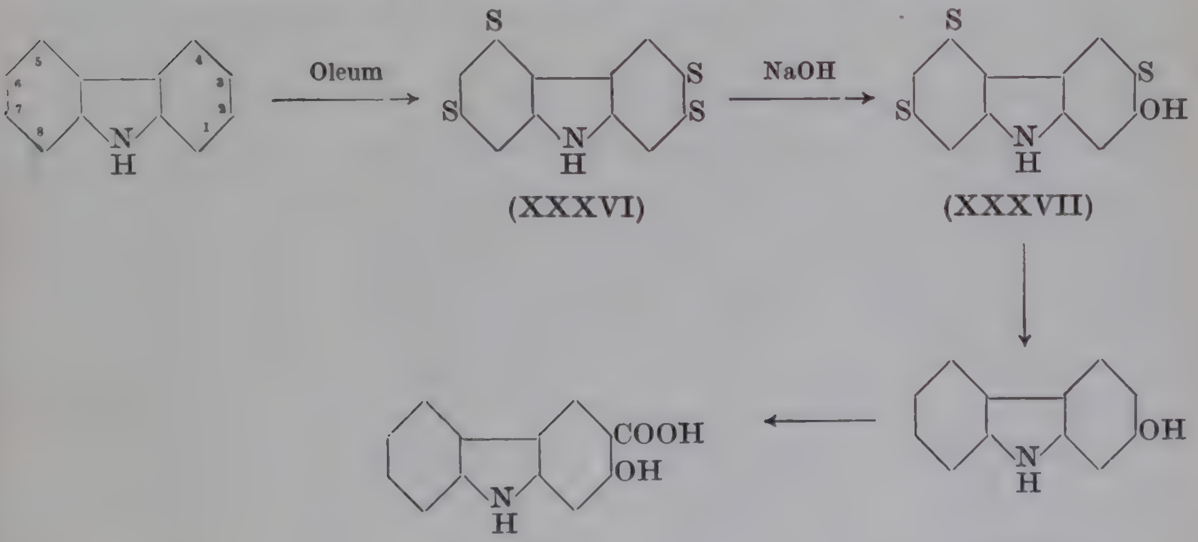


(XXXII) (XXXIII)

the 3-bromo compound by fusion with 16% caustic soda in presence of copper powder at 250° and 30–32 atm. pressure for about 18 hours (75–80% yield). 2-Hydroxycarbazole (XXXIV), required for the 3-carboxylic acid (XXXV), is prepared from carbazole by a circuitous method (Chart 7).[8, 13, 392, 393] At the sulfonation stage a mixture of (XXXVI) and the 1,3,6,8-tetrasulfonic acid is obtained; when the mixture is fused with

CHART 7

PREPARATION OF 2-HYDROXYCARBAZOLE-3-CARBOXYLIC ACID



(XXXVI) (XXXVII)

(XXXV) (XXXIV)

alkali under certain conditions, (XXXVII) is formed, the 1,3,6,8-acid being unaffected and removed in the filtrate during the isolation of (XXXVII). At the carboxylation stage, (XXXV) is admixed with about 12% of 2-hydroxycarbazole-1-carboxylic acid, which is valueless as a component for coupling with diazonium salts; (XXXV) has to be separated by salting out an alkaline solution. Another by-product in the Kolbe reaction on (XXXIV) is 4-hydroxydiphenyl-3-carboxylic acid. 2-Hydroxy-1′,2′-benzocarbazole-3-carboxylic acid (XXXVIII) is prepared[392] from 2-hydroxy-3-naphthoic acid by a carbazole synthesis (Chart 8). Sulfonation of hydroxynaphthoic acid at

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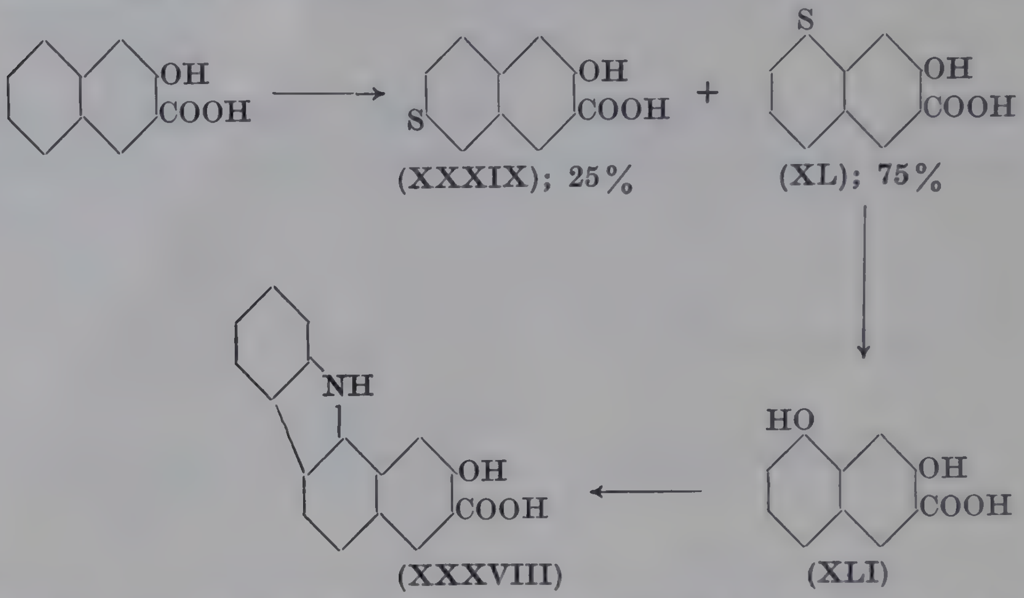
[129] See p. 83.
[8] See p. 50.
[13] See p. 50.
[392] IG, FP 754,224; DRP 603,945.
[393] *FIAT* 1313, I.

30° gives a 1:3 mixture of the 6- and 8-sulfonic acids (XXXIX) and (XL), together with a small amount of the 1-sulfonic acid, which is removed by diluting with water and boiling when desulfonation takes place. The two acids (XXXIX and XL) are then separated by fractionation of the potassium salts. Fusion of (XL) with caustic potash and 50% aqueous caustic soda at 250° in an autoclave gives 2,8-dihydroxynaphthalene-3-carboxylic acid (XLI). When (XLI) is heated successively with aqueous sodium sulfite and bisulfite and with sulfuric acid and phenylhydrazine at about 100°, a 64% yield of (XXXVIII) is obtained, with allowance for recovered (XLI). Separation of (XXXVIII) from unconverted (XLI) is effected by taking advantage of the solubility of (XLI) in sodium acetate solution.

CHART 8

PREPARATION OF 2-HYDROXY-1′,2′-BENZOCARBAZOLE-3-CARBOXYLIC ACID



Anthraquinone-2-carboxylic acid (m.p. 290–292°) and several of its derivatives are important intermediates for vat dyes. The general method of preparation is oxidation of the appropriate 2-methylanthraquinone with sodium dichromate and sulfuric acid or with potassium permanganate solution at about 90°. Examples are 1-chloroanthraquinone-2-carboxylic acid (m.p. 272°), 3-chloroanthraquinone-2-carboxylic acid (m.p. 285°), and 1-nitroanthraquinone-2-carboxylic acid (m.p. 285–287°). The anthraquinonecarboxylic acids are useful for the characterization of alcohols, since the esters are readily crystallizable and have high melting points.

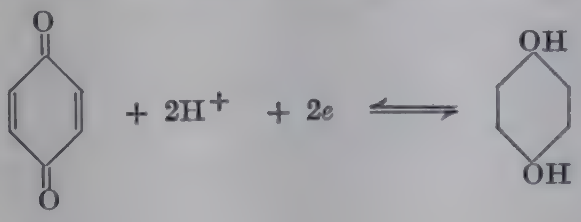
Acid chlorides. In addition to benzoyl chloride and the chlorobenzoyl chlorides prepared by partial hydrolysis of the corresponding benzotrichloride as mentioned earlier, various other acid chlorides (e.g., the chlorides of anisic acid, *m*- and *p*-nitrobenzoic acid) are used for acylating amines (e.g., J-acid, H-acid, the aminoanthraquinones). These acid chlorides are usually prepared by reaction of the acid with an equal weight of thionyl chloride at 100° until sulfur dioxide and hydrogen chloride are no longer evolved. Purification is then effected by vacuum distillation. The chlorides of isophthalic and terephthalic acid can be obtained directly from the xylenehexachlorides or the acid can be treated with twice its weight of thionyl chloride in a solvent such as *o*-dichlorobenzene until a clear solution is obtained, which usually takes several days.[10]

The addition of one equivalent of pyridine enables the preparation of acid chlorides by means of thionyl chloride to be carried out at room temperature.[394]

QUINONES

With the exception of *p*-benzoquinone (I), chloranil, and acenaphthenequinone, the quinones used as intermediates are anthraquinone and its derivatives, which are important intermediates for mordant, acid-mordant, and vat dyes. The preparation and properties[395] of the quinones are also of interest from the point of view of the quinonoid structure of dyes.[76]

Quinone (I; yellow prisms, m.p. 116°) is prepared technically by the oxidation of aniline with potassium dichromate, or manganese dioxide, and sulfuric acid. By adding aniline sulfate solution to a mixture of pyrolusite (of manganese dioxide content corresponding to 120–130% of the theoretically required amount) and dilute sulfuric acid below 10° during several hours and steam-distilling the product, quinone of very high purity can be obtained.[396] Processes for the electrolytic oxidation of benzene to *p*-benzoquinone and hydroquinone have been described.[397] Although hydroquinone is manufactured from quinone, a convenient laboratory method[398, 399] for the preparation of quinone is oxidation of the commercially available hydroquinone. It has a characteristic odor and is volatile in



(I)

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[10] See p. 50.

[394] Human and Mills, *Nature* **158**, 877 (1946); Carré and Libermann, *Compt. rend. acad. sci. U.R.S.S.* **199**, 1422 (1934).

[395] For an excellent account of the chemistry of the quinones, see Fieser and Fieser, Organic Chemistry, Heath, Boston, 1950.

[76] See p. 69.

[396] Carus, USP 2,144,424.

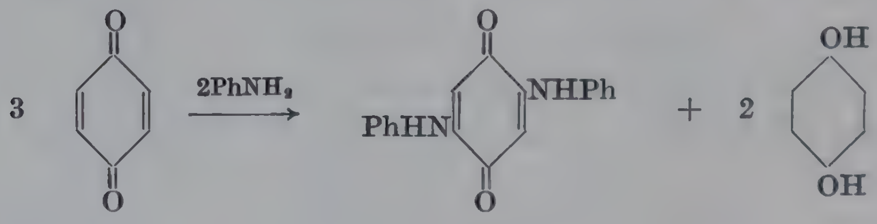
[397] *E.g.*, Palfreeman and Knibbs, BP 430,572; Horrobin, New, and ICI, BP 556,166.

[398] Vliet, *OSCV* I, p. 482.

[399] Underwood, Jr. and W. L. Walsh, *ibid* II, p. 553.

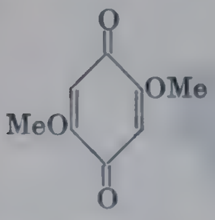
steam. As a diketone, it reacts with hydroxylamine to form a monoxime and a dioxime. On treatment of an aqueous suspension with sulfur dioxide a green color develops owing to formation of quinhydrone (lustrous green needles, m.p. 171°), a molecular complex of quinone and hydroquinone; by further treatment with sulfur dioxide the green color disappears and hydroquinone is obtained. The use of quinone as an intermediate is for the preparation of hydroquinone. Reduction of quinone to hydroquinone proceeds quantitatively, and is reversible. Each quinone-hydroquinone system has a characteristic reduction-oxidation ("redox") potential, and redox potential data are of value in studying the properties of anthraquinonoid vat dyes. The normal potential for the *p*-benzoquinone-hydroquinone system is 0.699 v.; quinhydrone can be utilized for determining the pH of solutions which are not more alkaline than pH 8.

Many quinones give characteristic colorations with aqueous alkali and with concentrated sulfuric acid. They undergo reduction and addition reactions more readily than open chain α,β-unsaturated ketones. Three types of addition reactions can be carried out. Reduction to the corresponding hydroquinone and the interaction of quinonediimide with aniline to form 4,4′-diaminodiphenylamine are examples of direct 1,4-addition.



(II)

When hydrogen chloride acts on quinone in chloroform solution, the product is 2-chlorohydroquinone, an indirect 1,4-addition taking place. An example of the third type is the action of aniline on quinone which leads to 2,5-dianilino-1,4-benzoquinone (II). Similarly, methanol and zinc chloride give 2,5-dimethoxy-1,4-benzoquinone (III). Quinone reacts with diazonium salts to form 2-phenyl-1,4-benzoquinone (IV) in good yield,[400] and by use of diazotized *o*-chloroaniline the reaction can be utilized for the synthesis of dibenzofurans.



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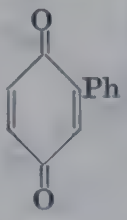

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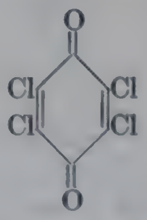
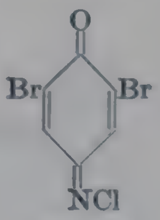


Chloranil



(V)

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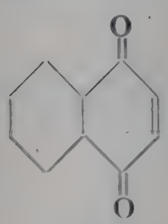
[400] Guenther, USP 735,432; Kvalnes, *JACS* **56**, 667, 670 (1934).

Chloranil (golden yellow crystals, m.p. 292°) is used in the preparation of direct cotton dyes of the dioxazine series which have high fastness to light and of some wool dyes of the Helindone class (IG). It is prepared[401, 402] from phenol or *o*-chlorophenol by chlorination at 60° to 2,4,6-trichlorophenol, admixed with a little of the 2,3,4-compound; the trichlorophenols are then dissolved in a mixture of sulfuric acid monohydrate and chlorosulfonic acid at 85–90°, and treated with chlorine until a sample diluted with water gives chloranil with a melting point of 290–294° (yield 95%). Chloranil can be produced directly from tri-, tetra, or pentachlorophenol, or their mixtures, in sulfuric acid by the action of chlorine at 90–130°.[403] Another process is to treat aniline (46.5 g.; 0.5 mole) in 70% sulfuric acid (600 g.) with chlorine for 8 hours at 110°; when 202 g. chlorine has reacted, the mass is cooled and filtered, when chloranil is obtained in 91% yield.[403] Chloranil is a useful reagent for the preparation of other derivatives of quinone and hydroquinone, and for oxidations, e.g., the dehydrogenation of hydroaromatic compounds.[404] The quinone derivative 2,6-dibromoquinone-4-chloroimide (V) is of value in carrying out the indophenol[141] test for phenols with a free *p*-position (blue color on adding the reagent to an alkaline solution of the phenol); it is prepared by bromination of *p*-nitrophenol to 2,6-dibromo-4-nitrophenol, reduction to the amine, and oxidation of the aminophenol with sodium hypochlorite.[405]

Naphthoquinones. Three naphthoquinones, α- or 1,4 (VI), β- or 1,2 (VII), and 2,6 (VIII) are known. Only (VI) is used as a dye intermediate, and its derivatives also occur in nature as vitamin K and as plant coloring matters. 2-Methyl-1,4-naphthoquinone (Menadione), readily obtained by the oxidation of β-methylnaphthalene with chromic acid, is used as a substitute for natural vitamin K_1, the simpler synthetic substance being more than twice as potent on a weight basis. 1,4- and 1,2-Naphthoquinones are



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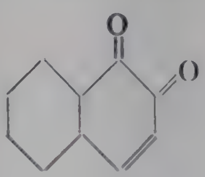

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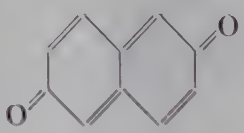

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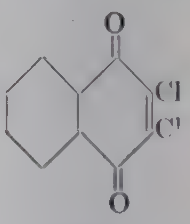

(IX)

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[401] *BIOS* **960.**

[402] *BIOS* **271.** See also Gallatti, *Ann. chim. applicata* **22,** 602 (1932).

[403] Dow Chem. Co., USP 2,414,008; See also Fletcher, USP 2,422,089; 2,422,229; BP 588,642.

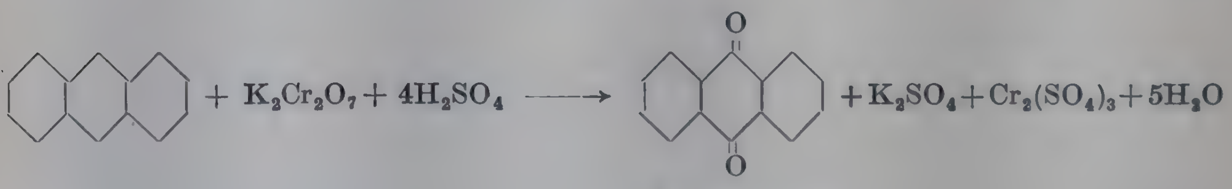
[404] Arnold and Collins, *JACS* **61,** 140 (1939); Arnold, Collins, and Zenk, *ibid.* **62,** 983 (1940); Barclay and Campbell, *JCS* 530 (1945).

[141] See p. 88.

[405] Hartman, Dickey, and Stampfli, *OSCV* II, p. 173, 175.

best prepared by oxidation of the corresponding aminonaphthols;[406] the 2,6-compound is obtained by oxidation of 2,6-dihydroxynaphthalene with lead peroxide.[407] Chlorination of 1,4-naphthoquinone in nitrobenzene solution[9] at a temperature gradually increasing from 15° to 96° gives 2,3-dichloro-1,4-naphthoquinone (IX), which is a potent fungicide[408] and a minor dye intermediate; (IX) (golden yellow needles, m.p. 193°) can also be prepared by sulfonation of *a*-naphthylamine, followed by chlorination.[409] Sodium 1,2-naphthoquinone-4-sulfonate gives a pink color with indole in chloroform solution (Herter's reaction).

Anthraquinone (pale yellow prisms or needles, m.p. 286°, b.p. 377°) is among the first few intermediates in the scale on which it is produced. There are two methods of preparation, of which one is the oxidation of anthracene. A well-established oxidizing agent for this purpose is sodium or potassium dichromate in presence of sulfuric acid; but oxygen in presence of vanadium pentoxide as catalyst, nitric acid, and other oxidizing agents can be employed.[399] The purer the anthracene, the simpler it is to purify the anthraquinone; anthracene containing paraffins and other impurities yields an anthraquinone which is difficult to filter. Pyridine-washed anthracene of 95% purity is suitable, and for dichromate oxidation it is necessary to use it in a finely dispersed state as the wet paste obtained by sublimation with superheated steam at 200° and condensation by contact with a spray of water. Dilute sulfuric acid is added in the course of several hours to a boiling mixture of dichromate solution and anthracene; the proportions are indicated in the equation. Crude anthraquinone is purified by heating with twice its weight of concentrated sulfuric acid at 100–110°, which sulfonates impurities such as phenanthraquinone, acridine and carbazole; anthraquinone is then precipitated by means of boiling water and finally sublimed. An air oxidation process was used by the IG at Ludwigshafen.[410] A mixture of air and steam, the latter being necessary to prevent spontaneous ignition of the anthracene and to retard oxidation


+ $K_2Cr_2O_7$ + $4H_2SO_4$
O
O
+ K_2SO_4 + $Cr_2(SO_4)_3$ + $5H_2O$

Anthraquinone

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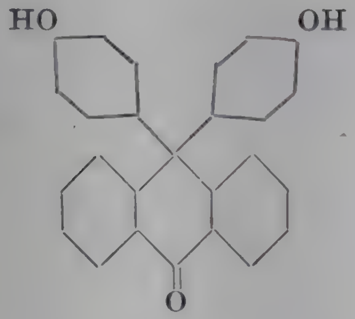
[406] Fieser, *ibid.* I, p. 383; II, p. 430.
[407] Willstätter and Parnas, *Ber.* **40**, 1411, 3971 (1907).
[9] See p. 50.
[408] Ter Horst and Felix, *Ind. Eng. Chem.* **35**, 1255 (1943).
[9] Ullmann and Ettisch, *Ber.* **54**, 259 (1921). See also Ref. 403.
[399] See p. 153.
[410] *BIOS* **1148**.

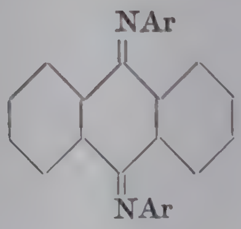
beyond the desired stage, is heated to 260° and passed through molten 93% anthracene. The air-steam-anthracene vapor preheated to 318° then enters a contact furnace in which beds of iron vanadate in 5 mm. grains are carried on nine perforated iron plates. The temperature in the furnace varies from 320–390°. The air containing anthraquinone enters scraper towers in which the anthraquinone separates (purity 98.6–99.9%; yield 82%).

Properties of anthraquinone. Anthraquinone is remarkable for its stability to heat and to oxidizing agents. It can be heated with concentrated sulfuric acid to high temperatures without decomposition, sulfonation beginning only above 200°. The benzenoid resonance of the two outer rings tends to isolate the carbonyl groups, which in their properties are therefore intermediate between ketonic and quinone groups. As a ketone, anthraquinone forms a monoxime when heated with hydroxylamine hydrochloride at 180°, but it does not react with phenylhydrazine, although a monophenylhydrazone can be obtained from meso-dibromoanthrone heated with phenylhydrazine. One or both the carbonyl groups condense with primary amines and phenols at a high temperature to yield compounds of the type (X) and (XI). Anthraquinone is not reduced by sulfurous acid as benzoquinone is; but it dissolves in aqueous caustic soda and sodium hydrosulfite to a blood-red solution of the disodium salt of the 9,10-dihydro or leuco compound (anthrahydroquinone). Owing to the deactivating effect of the carbonyl groups, anthraquinone is very difficult to substitute, sulfonation with 25% oleum requiring a temperature of about 140°. For this reason and also because of the ready replaceability of the sulfonic groups in the anthraquinone series, anthraquinonesulfonic acids are useful primary intermediates from which other anthraquinone derivatives, particularly chloro compounds and amines, are prepared.

(X)



(XI)



When the red solution (or " vat ") obtained by reduction of anthraquinone with caustic soda and sodium hydrosulfite solution is aerated, anthraquinone is reprecipitated. This is a fundamentally important reaction which enables the use of anthraquinone derivatives as vat dyes, and it can be used for the estimation of anthraquinone and its derivatives.

Further reduction of the anthraquinone vat by means of zinc dust leads first to a yellow solution of the sodium salt of anthranol (9-hydroxyanthracene), and ultimately results in complete decolorization and formation of anthracene. The reduction of anthraquinone and its derivatives to the corresponding anthracenes by prolonged treatment with zinc and alkali (usually ammonia) provides a convenient route to many anthracene derivatives (e.g., α-and β-anthrol), since the anthraquinone derivatives are readily obtainable by suitable substitution of anthraquinone or by the phthalic anhydride synthesis. Anthranol in alkaline solution can be coupled with diazonium salts at a low temperature, but it is unstable and rapidly tautomerizes to anthrone (pale yellow, m.p. 156°), which however is best prepared by reduction of anthraquinone in boiling glacial acetic acid solution with tin and hydrochloric acid.[411] Anthrone can also be synthesized by reduction of *o*-benzoylbenzoic acid with zinc dust and aqueous caustic soda, which proceeds quantitatively to *o*-benzylbenzoic acid (XII), followed by cyclization of (XII) with sulfuric acid[412] or hydrofluoric acid.[413] The action of pyridine (an enolizing solvent) and acetic anhydride on anthrone gives anthranyl acetate (9-acetoxyanthracene; XIII).

A reaction of anthrone of great technical importance is its condensation with acrolein (from glycerol and sulfuric acid) to form benzanthrone; and anthrone can undergo various other condensations leading to 1,9-substituted heterocyclic derivatives of anthraquinone.

Anthrahydroquinone (very unstable brownish yellow crystals, m.p. 180°) is tautomeric with oxanthrone (oxanthranol; colorless, m.p. 167°); in alcoholic hydrochloric acid the equilibrium mixture contains 97% anthrahydroquinone and 3% oxanthrone. The latter has been prepared as a colorless nonfluorescent substance by hydrolysis of 10-bromo-9-anthrone with water or by careful oxidation of anthracene in aqueous acetone with bromine. Anthracene is oxidized by lead tetracetate, first to a mixture of the *cis*- and *trans*- forms of 9,10-diacetoxy-9,10-dihydroanthracene (XIV), both of which readily lose acetic acid with formation of anthranyl acetate (XIII). By further oxidation two more acetoxyl groups are added to give an intermediate which loses acetic anhydride to yield oxanthrone acetate (XV).[414] These interrelationships of anthracene, anthraquinone and the intermediate stages in the conversion of one to the other are shown in Chart 9.

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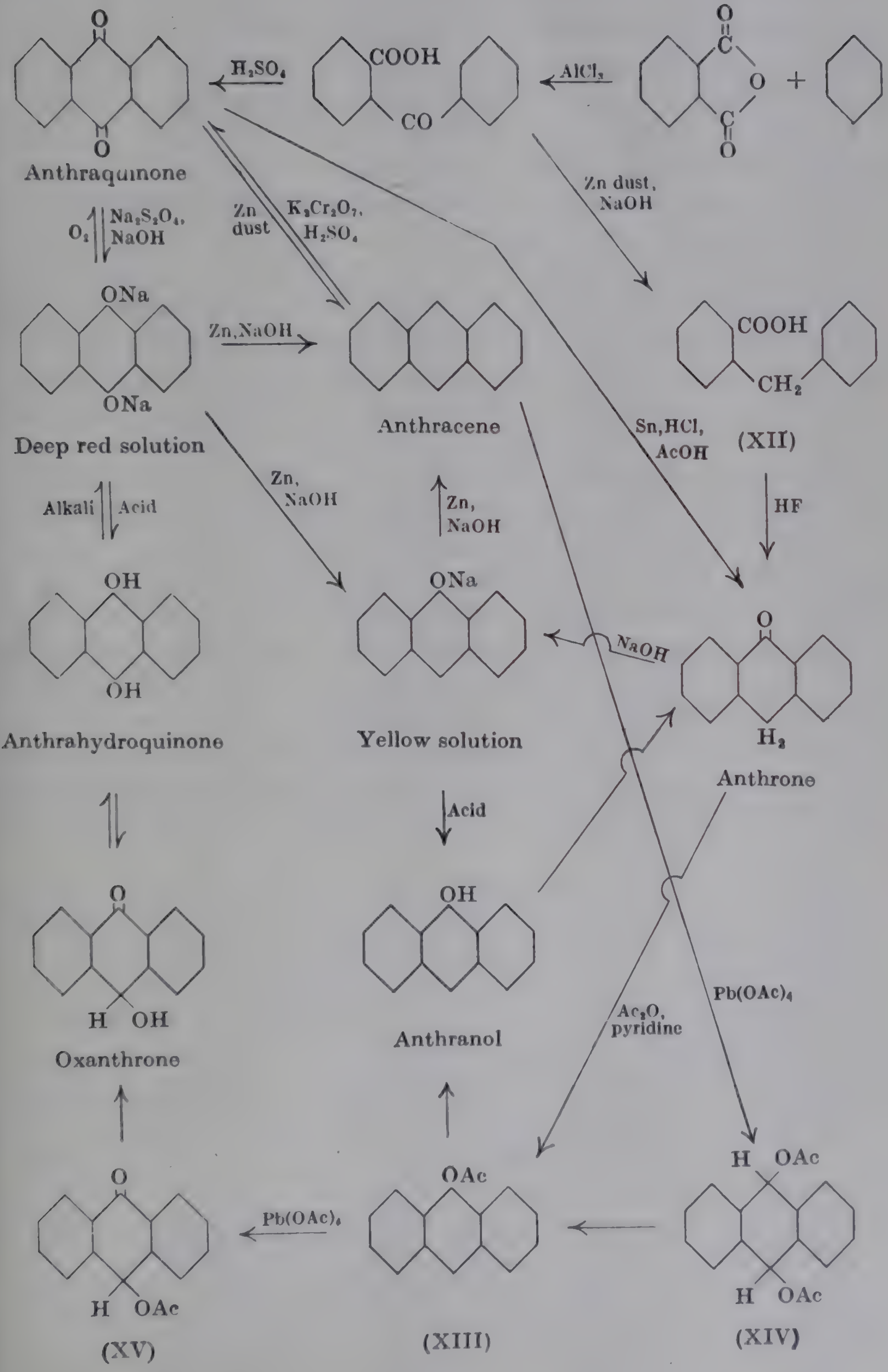
[411] Meyer, *OSCV* I, p. 60.

[412] Ullmann, *Ann.* **291,** 23 (1896); Barnett, Cook, and Nixon, *JCS* 504 (**1927**).

[413] Fieser and Hershberg, *JACS* **61,** 1278 (1939).

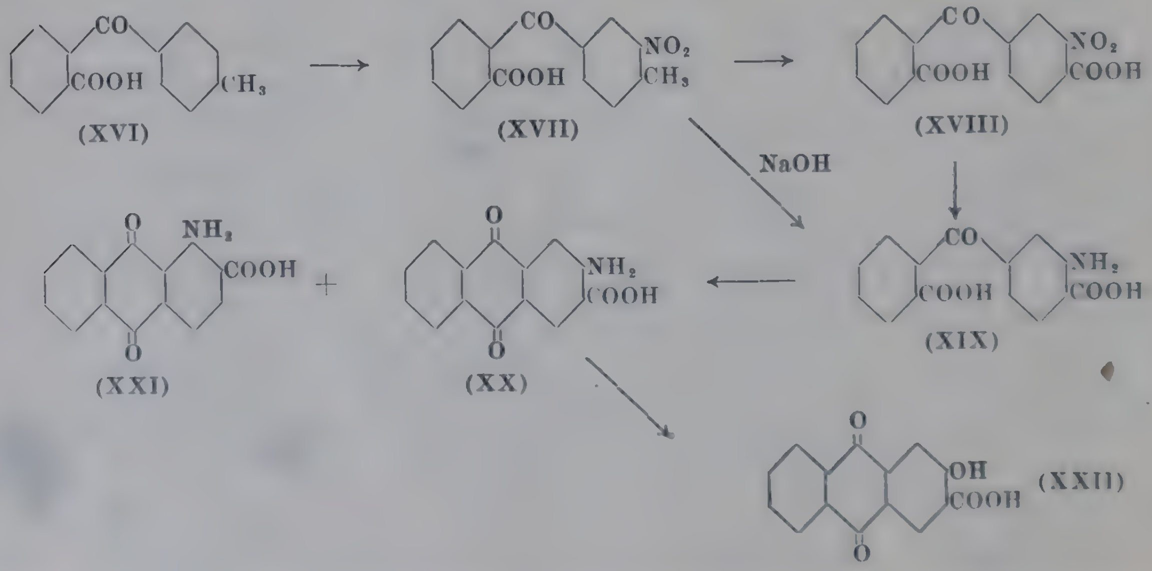
[414] Fieser and Putnam, *JACS* **69,** 1038 (1947).

CHART 9


Anthraquinone
H₂SO₄
COOH
CO
AlCl₃
O
+
Zn dust, NaOH
O₂
Na₂S₂O₄, NaOH
Zn dust
K₂Cr₂O₇, H₂SO₄
ONa
Zn,NaOH
COOH
CH₂
Deep red solution
Anthracene
Sn,HCl, AcOH
(XII)
Alkali
Acid
Zn, NaOH
Zn, NaOH
HF
OH
Anthrahydroquinone
ONa
NaOH
Yellow solution
H₂
Anthrone
Acid
O
H OH
Oxanthrone
OH
Anthranol
Ac₂O, pyridine
Pb(OAc)₄
Pb(OAc)₄
H OAc
OAc
(XV)
(XIII)
(XIV)

Phthalic anhydride synthesis of anthraquinone. Anthraquinone, β-chloroanthraquinone, and β-alkylanthraquinones can be synthesized by the condensation of benzene or the appropriate derivative with phthalic anhydride in presence of aluminium chloride and cyclization of the *o*-benzoylbenzoic acid by the action of concentrated sulfuric acid or of oleum at about 100° for a few hours. For the β-alkylanthraquinones, such as β-methylanthraquinone which is an important intermediate, this synthetic route is the only one available. Anthraquinone itself is manufactured in the United States by this method.

***p*-Toluoylbenzoic acid** (XVI), obtained by the condensation of phthalic anhydride with toluene, is largely used, since it gives 2-methylanthraquinone by cyclization[415] and also lends itself to the preparation of a variety of anthraquinone derivatives. Thus by nitration to (XVII), oxidation to the carboxylic acid (XVIII), reduction to (XIX), and cyclization, a mixture of 2-aminoanthraquinone-3-carboxylic acid (XX) and 1-aminoanthraquinone-2-carboxylic acid (XXI) is obtained in a proportion of about 7 : 3. 2-Hydroxyanthraquinone-3-carboxylic acid (XXII) can be obtained from (XX) by diazotization and hydrolysis. Another route to (XXII), together with the 1-carboxylic acid, is the action of caustic soda on (XVII) at 95°, which results in isomerization to 3-aminobenzophenone-2′,4-dicarboxylic acid (XIX), converted by diazotization into 4-*o*-carboxybenzoylsalicylic acid, which is then cyclized. A third route to (XXII), also starting from (XVI) and proceeding through a chloro derivative, has been mentioned earlier, the interest in (XXII) being its reducibility to 2-hydroxyanthracene-3-carboxylic acid, an intermediate for Naphtol AS-GR. Sulfonation of (XVI) followed by cyclization gives 3-methylanthraquinone-



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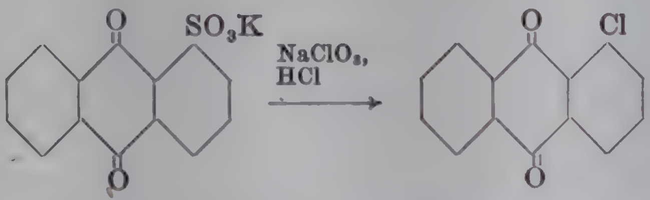
[415] Fieser, *OSCV* I, pp. 517, 353.

2-sulfonic acid; if this is nitrated, the sulfonic group replaced by chlorine by treating the aqueous solution with sodium chlorate, and the nitro group reduced by sodium sulfide, the products[416] are 6-chloro-1-amino-7-methylanthraquinone and 7-chloro-1-amino-6-methylanthraquinone.

2-Ethylanthraquinone,[417] used by the IG in a new process[418] for the production of hydrogen peroxide, which is formed simultaneously with the anthraquinone when the corresponding anthrahydroquinone is oxidized by air, is made by the condensation of ethylbenzene with phthalic anhydride in chlorobenzene as solvent at 35–40°, followed by cyclization with 8% oleum at 85–87°. In other cases however the liquid reactant itself (benzene, toluene, chlorobenzene) can be conveniently employed as the solvent.

Chloroanthraquinones. α-Chloroanthraquinone (bright yellow needles, m.p. 162.5°) is obtained[419] in 97–98% yield by adding a 20% solution of sodium chlorate (100 cc.) in 3 hours to a solution of potassium anthraquinone-α-sulfonate (20 g.) in concentrated hydrochloric acid (85 cc.) and water (500 cc.) at the boil, and boiling the mixture for a further hour.[420] In the conversion of an anthraquinonesulfonic acid into the corresponding chloro compound by means of sodium chlorate and acid, production is increased 4–5 times when the volumes of the reaction mixtures are reduced and a solvent such as *o*-dichlorobenzene or nitrobenzene is added.[421] β-Chloroanthraquinone can be similarly prepared from silver salt, but synthesis from chlorobenzene and phthalic anhydride is preferred.[422] In the preparation of 3′,4′-dichloro-2-benzoylbenzoic acid from *o*-dichlorobenzene and phthalic anhydride, the maximum yield is 80%. Cyclization of the keto acid with sulfuric acid gives a mixture of 1,2- and 2,3-dichloroanthraquinones (13 and 87%).[422] Nuclear substituted chlorine atoms in the anthraquinone series are more labile than those in similar benzene and naphthalene derivatives; chlorine in the α-position is more readily replaceable, for instance by reduction, than one in the β-position. Chlorine in



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[416] Wuertz, Gottlieb, and du Pont, USP 2,329,023.

[417] *BIOS* 917.

[418] *CIOS* Item No. 22, File No. XIX–4.

[419] Baeyer, DRP 205,195; BASF, DRP 228,876; Ullmann and Ochsner, *Ann.*, **381**, 1 (1911); Scott and Allen, *OSCV* II, p. 128.

[420] The replacement of SO_3H by Cl in the chloroanthraquinonesulfonic acids has been studied by Lauer, *J. prakt. Chem.* (ii) **136**, 1 (1933).

[421] Weinmayr, USP 2,417,027.

[422] Groggins *et al.*, *Ind. Eng. Chem.* **25**, 1083 (1933).

the α-position can usually be replaced by hydrogen by heating with potassium acetate in nitrobenzene solution in presence of a trace of copper powder; with excess of copper powder and in the absence of potassium acetate, the corresponding 1,1′-dianthraquinonyl is formed. In α, β-dichloroanthraquinones the α-chlorine is more easily replaceable, e.g., by amino and anthraquinonylamino groups, and 6-chloro-1-aminoanthraquinone and its derivatives can be conveniently prepared by this method. An important reaction of 1-chloroanthraquinones is the replaceability of chlorine by hydroxyl on treatment with warm concentrated sulfuric acid. Thus the condensation of phthalic anhydride with *p*-chlorophenol in presence of aluminium chloride, followed by cyclization in the usual manner with sulfuric acid, gives quinizarin (1,4-dihydroxyanthraquinone), and not 1-chloro-4-hydroxyanthraquinone. The reaction proceeds smoothly in one operation on heating phthalic anhydride, *p*-chlorophenol, concentrated sulfuric acid, and boric acid at 200°, and is the technical method for preparing quinizarin, a very important intermediate.[423] An interesting preparation of 2,3-dichloroanthraquinone, which shows the greater lability of chlorine in the α-positions, is the action of zinc dust and ammonia or of caustic soda and sodium hydrosulfite solution on 1,2,3,4-tetrachloroanthraquinone (m.p. 191°), which is readily obtainable by the condensation of tetrachlorophthalic anhydride and benzene. 1,4,5,8-Tetrachloroanthraquinone (m.p. 342°) can be prepared by the prolonged chlorination of anthraquinone in oleum; or by replacement of the sulfonic groups in 1,8-dichloroanthraquinone-4,5-disulfonic acid or 1,5-dichloroanthraquinone-4,8-disulfonic acid by the usual method of treating the aqueous solution of the sodium salt with nascent chlorine; or by dinitrating 1,5-dichloroanthraquinone and replacing the nitro groups by chlorine, which occurs when chlorine is passed through a boiling solution in nitrobenzene. When 2-methylanthraquinone is chlorinated at 5° in 5% oleum in presence of iodine, the product is a mixture of the 1- and 3-chloro compounds, which are separated by heating with aqueous sodium sulfite in presence of copper sulfate and sodium carbonate at 120° in an autoclave for 15 hours. The 1-chloro compound is obtained from the cooled solution by filtration.[7]

The phthalic anhydride route to anthraquinone derivatives has the great advantage that the orientation of the substituents is usually unambiguous. Numerous anthraquinone derivatives have therefore been prepared by this method, and some examples[424] are anthraquinonesulfonic acids (good yield),[425] 1,3-dichloro- and 2,3,6-trichloroanthraquinones,[426] 1-methylanthraquinone and many of its derivatives,[427] 5,7-diamino-2-methylanthraquinone,[428] 4,6- and 4,7-dihydroxy-2-methylanthraquinones,[429] and 1-chloro-3-methoxy-2-methylanthraquinone.[430] β-Nitrophthalic anhydrides condense readily with hydrocarbons in the Friedel-Crafts reaction. Thus 4-nitrophthalic anhydride gives with toluene a mixture of 4- and 5-nitro-2-toluoylbenzoic acids, which by reduction and ring closure yield a mixture of 6- and 7-amino-2-methylanthraquinone.[431] 4-Chloro-5-nitrophthalic anhydride with benzene and chlorobenzene leads to 3-chloro-2-aminoanthraquinone and probably a mixture of 3,6- and 3,7-dichloro-2-aminoanthraquinones.[432] Condensation of phthalic anhydride with 2-aminochrysene in presence of aluminium chloride gives an anthraquinone derivative probably constituted as (XXIII). Similar condensations can be effected with 4-aminofluoranthene and 3-aminopyrene.[433]

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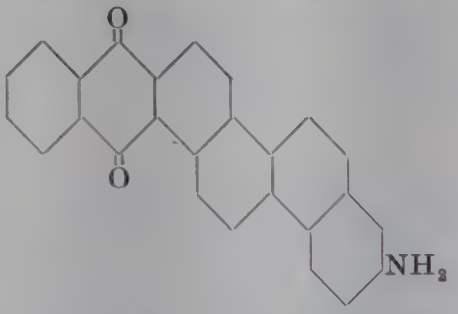
[423] Baeyer and Caro, *Ber.* 8, 152 (1875); Reynolds and Bigelow, *JACS* **48**, 420 (1926); *OSCV* I, p. 476; National Aniline Co., USP 1,845,632; 1,886,237; Dodd, Sprent, and United Alkali Co., BP 245,584 ; see also Gubelmann and Weiland, USP 1,790,915.

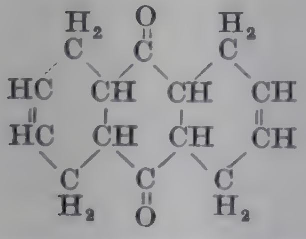
[7] See p. 50.

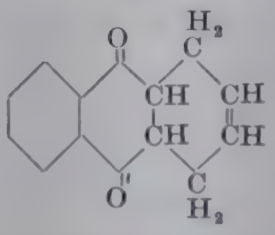


(XXIII)

Anthraquinone synthesis by the Diels-Alder reaction. An interesting route to anthraquinone and its derivatives, which however has no technical value, is the Diels-Alder reaction on *p*-benzoquinone and 1,4-naphthoquinone, which give with butadiene the adducts (XXIV) and (XXV).[434] Oxidation of (XXIV) and (XXV) by means of chromic acid

(XXIV)





(XXV)

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[424] See also Thomas, Anhydrous Aluminium Chloride in Organic Chemistry, Reinhold, New York, 1941.

[425] Schwenk and Waldmann, *Angew. Chem.* **45,** 17 (1932).

[426] Goldberg, *JCS* 2829 **(1931)**; *ibid.* 73 **(1932)**; see also Lauer, *J. prakt. Chem.* (II), **136,** 1 (1933).

[427] Mayer and Stark, *Ber.* **64,** 2003 (1931).

[428] Mitter and Goswami, *J. Indian Chem. Soc.* **8,** 685 (1931).

[429] Mitter and Chatterji, *ibid.* **8,** 783 (1931).

[430] Mitter and Biswas, *Ber.* **65,** 622 (1932).

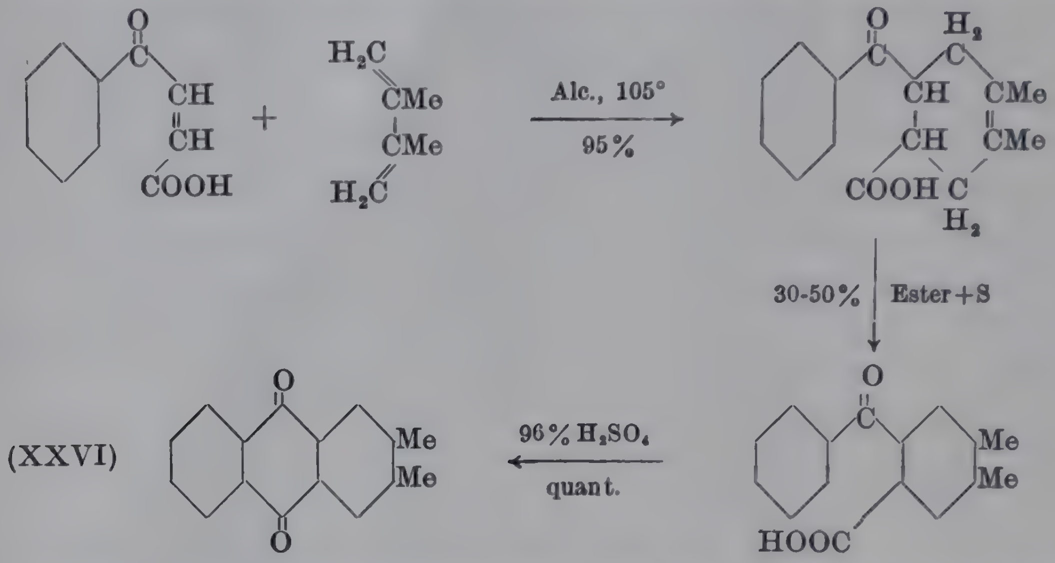
[431] Hayashi and Nakayama, *J. Soc. Chem. Ind. Japan* **37,** 238B (1934).

[432] ICI, BP 427,251.

[433] IG, BP 511,965; 514,115.

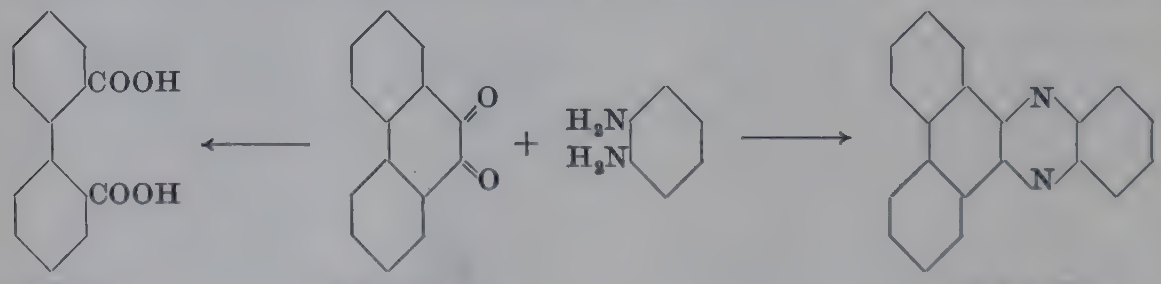
[434] Diels and Alder, *Ann.* **460,** 98 (1928); BP 340,509; 341,553; DRP 494,433; Carothers *et al.*, *JACS* **53,** 4203 (1931).

in glacial acetic acid or by passing air into the blood-red solution in alcoholic alkali yields anthraquinone. Aromatic hydrocarbons and maleic anhydride by the Friedel-Crafts reaction give aroylacrylic acids, which with butadienes yield tetrahydro-2-benzoylbenzoic acid derivatives, convertible to anthraquinones as indicated.[435] 2,3-Dimethylanthraquinone (XXVI) is obtained in 95% yield by the Diels-Alder reaction between 1,4-naphthoquinone and 2,3-dimethyl-1,3-butadiene, followed by aeration of the alkaline solution of the adduct.[436]



(XXVI)

Phenanthraquinone (XXVII; orange plates, m.p. 206°), prepared from phenanthrene by oxidation with potassium dichromate and 96% sulfuric acid, is useful for identifying *o*-diamines, with which it condenses to form quinoxalines (XXVIII). Further oxidation of (XXVII) gives diphenic acid (XXIX).



(XXIX) (XXVII) (XXVIII)

Acenaphthenequinone (XXX; yellow needles, m.p. 261°). When acenaphthene is oxidized in the same manner as anthracene or phenanthrene, a mixture of the quinone (XXX, 40–60% yield) and naphthalic acid (XXXI) is obtained,[437] which is readily separated by dissolving (XXXI) in sodium carbonate solution. A good method[6] for the preparation of (XXX) is to treat acenaphthene (1.2 parts) in alcohol (4.27 parts) containing hydrogen chloride (0.2 part) at 70–80° with ethyl nitrite generated from alcohol (0.95 part), sodium nitrite (1.7 parts), and sulfuric acid. The dioxime (XXXII) is filtered after neutralization of the reaction mixture and hydrolyzed to (XXX) at 98° for a few hours with 14% sulfuric acid (1.7 parts) and 40% formaldehyde (2.5 parts). The yield is 62%. Acenaphthenequinone as well as phenanthraquinone can be purified by dissolving in aqueous sodium bisulfite and reprecipitating by acidification.

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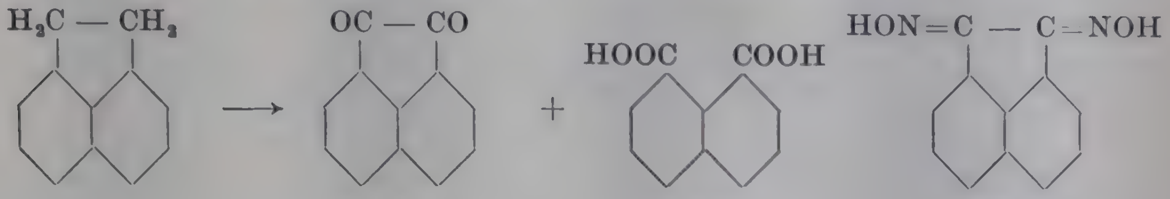
[435] Fieser and Fieser, *ibid.* **57,** 1679 (1935).

[436] Allen and Bell, *Org. Syntheses* **22,** 37 (1942).

[437] Maxwell and Allen, *ibid.* **24,** 1 (1944).

[6] See p. 50.



(XXX) (XXXI) (XXXII)

Naphtholsulfonic Acids

Naphtholsulfonic acids can be prepared by (*a*) sulfonation of the naphthols, (*b*) partial hydrolysis of naphthalene polysulfonic acids, and (*c*) replacement of the amino group in naphthylaminesulfonic acids.

α-Naphthol monosulfonic acids. Sulfonation of α-naphthol with concentrated sulfuric acid at about 90° gives the 2-sulfonic acid (Schaeffer and Baum acid), which is used in the preparation of 2,4-dinitro-1-naphthol, together with the 4-, 2,4- and probably some 2,7-acids; the potassium salt of the desired acid can be separated by the addition of potassium chloride solution. A good method is to heat the sodium salt of 1-naphthol-4-sulfonic acid (NW-acid) at 160–170°.[438] When α-naphtholsulfonic acids are nitrated, sulfonic groups in the 2- and 4-positions are replaced by nitro groups. 1-Naphthol-3-sulfonic acid (Armstrong and Wynne acid) is prepared by heating 1-naphthylamine-3-sulfonic acid with 10 times its weight of 0.25% sulfuric acid in an autoclave at 10 atm. pressure for 24 hours. Another method is to treat the 3,8-disulfonic acid with boiling dilute sulfuric acid at 120°, when the α-sulfonic group is eliminated; reduction with sodium amalgam or Raney nickel can be used for the same purpose. Desulfonation usually proceeds more readily in the α- than in the β-position. 1-Naphthol-4-sulfonic acid (Nevile and Winther or NW-acid) is an important intermediate prepared by refluxing an aqueous solution of sodium naphthionate and sodium bisulfite for 24 hours.[439] Sulfonation of α-naphthol at about 50° also gives NW-acid together with 20% of isomeric acids, which can be separated by coupling with the calculated amount of diazotized aniline, since they couple more rapidly than NW-acid.

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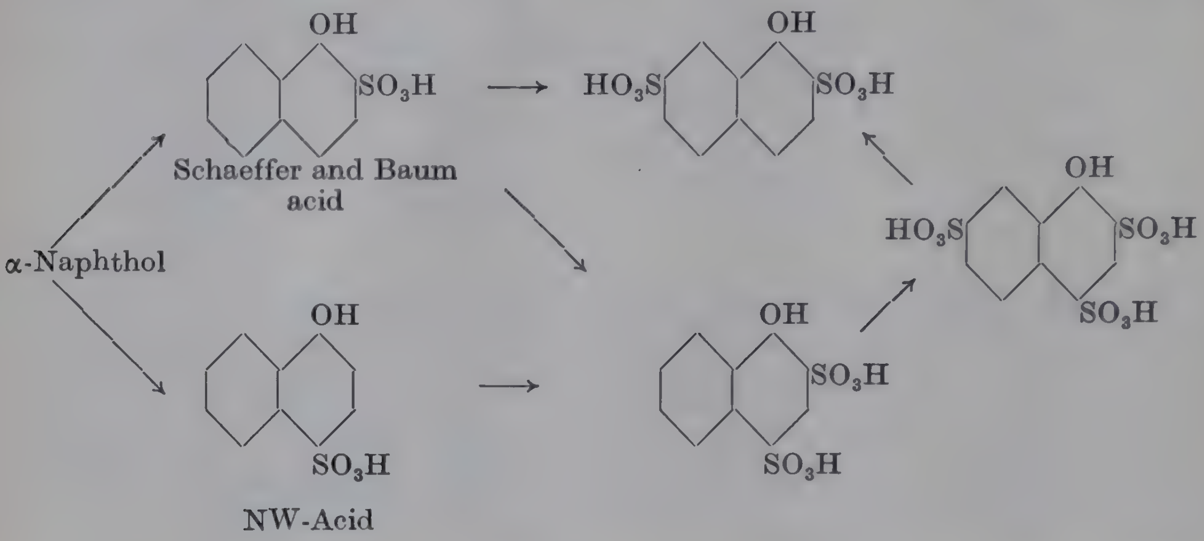
[438] Bayer, DRP 237,396.

[439] du Pont, USP 1,580,714.



Sulfonation of α-naphthol with chlorosulfonic acid in tetrachloroethane is stated to give NW-acid admixed with less than 2% of isomeric acids.[440] NW-Acid is said to be obtained in theoretical yield when 1-chloronaphthalene-4-sulfonic acid is heated with 5% caustic soda (3–4 moles) at 200° and 11–13 atm. for 7 hours.[441] 1-Naphthol-5-sulfonic acid (oxy-L-acid) is prepared by the alkali fusion of naphthalene-1,5-disulfonic acid under the conditions necessary for partial hydroxylation. 1-Naphthol-8-sulfonic acid is used in the form of the inner anhydride, naphthasultone (m.p. 154°), prepared by the action of nitrous acid on 1-naphthylamine-8-sulfonic acid (Peri-acid). Hydrolysis of naphthasultone with boiling caustic soda solution gives sodium 1-naphthol-8-sulfonate. Naphthasultone undergoes the Friedel-Crafts reaction with carboxyl and sulfonyl chlorides to give ketones and sulfones; thus with acetyl chloride and aluminium chloride naphthasultone 4-methyl ketone is obtained, which on hydrolysis with 30% aqueous caustic soda gives 4-acetyl-1-naphthol-8-sulfonic acid.[442] 4-Acyl derivatives of 1-naphthol-8-sulfonic acid are intermediates for chromable azo dyes.[443] 4-Chloromethylnaphthasultone is a useful intermediate.[443a]

α-Naphthol disulfonic acids. ε-Acid (1-naphthol-3,8-disulfonic acid), prepared from the corresponding naphthylamine, is used for making pink azo dyes. The more important 3,6-acid (Violet acid; Acid GR) is obtained by the careful alkali fusion of naphthalene-1,3,6-trisulfonic acid; as in the case of desulfonation the α-sulfonic group is preferentially attacked. Sulfonation of naphthasultone at 100° followed by treatment with alkali gives the disodium salt of 1-naphthol-4,8-disulfonic acid (δ-acid). The 4,6- and 4,7-disulfonic acids (Dahl acids) are prepared from the corresponding mixture of α-naphthylamine disulfonic acids. The 2,7-acid, useful as an intermediate for the preparation of Naphthol Yellow S, is a product of the direct sulfonation of α-naphthol with 2–3 times its weight of concentrated sulfuric acid at 125–130°, but it is difficult to separate from the other sulfonic acids which are simultaneously formed. Other methods of preparation start from the corresponding naphthylamine and from 1-naphthol-2,4,7-trisulfonic acid; in the latter case the sulfonic group in the α-position is eliminated by reduction with sodium amalgam.[444]

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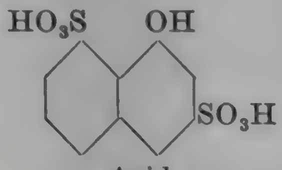
[440] British Dyestuffs Corp., BP 237,396.

[441] Vorozhtzov and Karlasch, *Anilinokrasochnaya Prom.* **4,** 545 (1934).

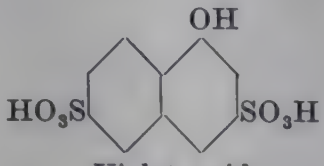
[442] Geigy, BP 575,285; Schetty, *Helv. Chim. Acta* **30,** 1650 (1947).

[443] Geigy, BP 599,867.

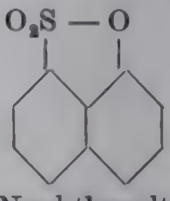
[443a] Geigy, USP 2,451,579.



ε-Acid



Violet acid



Naphthasultone

α-Naphthol trisulfonic acids. Sulfonation of α-naphthol with 50% oleum at 50° for 6 hours gives the 2,4,7-trisulfonic acid; the 2,4-sulfonic groups can be replaced by nitro groups as stated earlier, the product being the acid dye, Naphthol Yellow S. 1-Naphthol-3,6,8-trisulfonic acid is important as an intermediate for the preparation of chromotropic acid (1,8-dihydroxynaphthalene-3,6-disulfonic acid), and is prepared from the corresponding naphthylamine (Koch acid) by hydrolysis of the diazonium salt.

β-Naphthol monosulfonic acids are mainly prepared by sulfonation of β-naphthol. Sulfonation below 35° (a temperature of about −10° being used technically) gives chiefly (about 70%) the 1-sulfonic acid (Oxy-Tobias acid),[445] used for amination to Tobias acid. A better method for the preparation of Oxy-Tobias acid is sulfonation of β-naphthol in a suitable solvent. Its behavior towards diazonium salts is interesting: the sulfonic group is replaced, or more complex reactions occur with formation of phthalazines.[41] Concentrated sulfuric acid at 50–100° yields a mixture of the 6- and 8-sulfonic acids (Schaeffer acid and Crocein acid), the former predominating at the higher temperature. Schaeffer acid is obtained in 82% yield by heating β-naphthol with an equal weight of 98% sulfuric acid at 94–96° for 1–2 hours. The two acids can be salted out fractionally, Schaeffer salt separating first, or advantage may be taken of the fact that Crocein acid, on account of the sulfonic group in the 8-position, couples very slowly with diazonium salts. The scarlet azo dyes from Crocein acid are characterized by their brightness; similar dyes from Schaeffer acid

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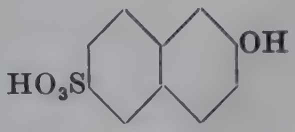
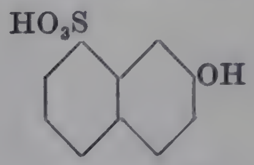
[444] Friedländer and Taussig, *Ber.* **30,** 1463 (1897).

[445] National Aniline Co., USP **1,913,748.**

[41] See p. 57.

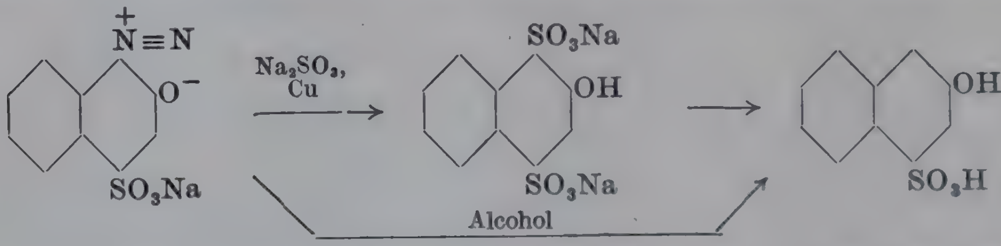


Schaeffer acid



Crocein acid

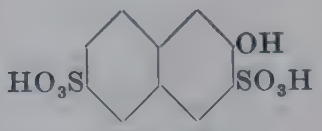
are maroon. 2-Naphthol-4-sulfonic acid (I) can be prepared from 2-naphthylamine-4,8-disulfonic acid by hydrolysis with dilute sulfuric acid under pressure or more conveniently by the alcohol or glucose reduction of diazotized 1-amino-2-naphthol-4-sulfonic acid.[446, 447] An interesting route to (I) is the preferential hydrolysis of the 1-sulfonic group in 2-naphthol-1,4-disulfonic acid, this unusual intermediate being obtained



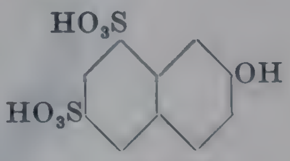
(I)

in good yield from sodium 1-diazo-2-naphthol-4-sulfonate when boiled with sodium sulfite solution in presence of copper powder and copper sulfite.[448] 2-Naphthol-7-sulfonic acid (F-acid) is prepared by the fusion of naphthalene-2,7-disulfonic acid with 25% aqueous caustic soda (2.5 parts) at 230–265° for 10 hours.

β-Naphthol disulfonic acids. The prolonged action of sulfuric acid on β-naphthol leads to two very important azo dye intermediates, R- and G-acids, which are also used for fast green acid triphenylmethane dyes (e.g., Wool Green S). The main product is R-acid, when β-naphthol is heated for several hours with thrice its weight of sulfuric acid at 110°;



R-Acid



G-Acid

R-salt separates on pouring the sulfonation mixture into brine, G-acid remaining in solution.[449] G-Acid can be separated from R-acid by precipitation of the former as the potassium salt. R-Salt is much less soluble in

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[446] Morgan and Jones, *J. Soc. Chem. Ind.* **42**, 97T (1923); Masschalk, *Bull. soc. chim. France* [4] **45**, 651 (1929).

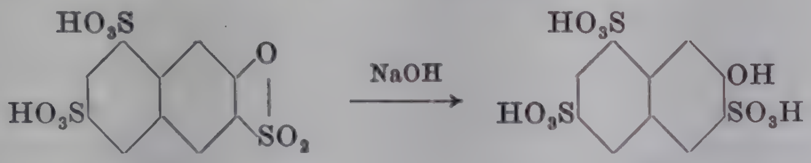
[447] See also Krebser and Vannotti, *Helv. Chim. Acta* **21**, 1221 (1938).

[448] Geigy, BP 485,971.

[449] National Aniline Co., USP 1,880,442; see also Calco, USP 1,701,259.

boiling alcohol than G-salt.[450] By sulfonating β-naphthol with 98% sulfuric acid at temperatures rising in controlled steps from 15° to 122°, R-salt can be obtained as the major end product, G-salt and Schaeffer salt being produced in quantities too small for recovery.[451] Sulfonation of β-naphthol with 3–4 parts of sulfuric acid at 60° for 48 hours or with monohydrate at 35° gives G-acid as the major product, together with R- and Schaeffer acids.[452] One method of removing the latter acids is to couple with a diazonium salt, G-acid reacting much more slowly.[453] R-Salt in presence of G-salt can be estimated by treatment with bromine water, the former alone forming the 1-bromo compound under prescribed conditions.[454] 2-Naphthol-3,7-disulfonic acid is formed by further sulfonation of F-acid. 2-Naphthol-5,7-disulfonic acid is prepared by heating 2-naphthylamine-5,7-disulfonic acid ("amido-J-acid") with dilute sulfuric acid under pressure. The 4,7- and 4,8-acids are obtained from the corresponding naphthylamines through the diazonium salts.

β-Naphthol trisulfonic acids. The 3,6,8-acid (II) is used as an intermediate, and is prepared by the sulfonation of β-naphthol with 40% oleum at about 120° or by the further sulfonation of G- or R-acid. The 2,3-sultone (III) is the product precipitated by dilution of the sulfonation mixture, and it is then converted into (II) by alkali treatment. A maximum yield of 50–60% of (II) can be obtained by sulfonation of β-naphthol at 130°.[455]



(III) (II)

Identification of the naphtholsulfonic acids. α- and β-Naphthol are first identified by desulfonation under suitable conditions; a general method is to dissolve the naphtholsulfonic acid in concentrated sulfuric acid, dilute with water to obtain a solution of b.p. 120–130°, and boil until complete desulfonation is effected. Partial desulfonation by means of boiling dilute sulfuric acid, sodium amalgam, alkali-hydrosulfite or Raney nickel shows differences between α- and β-sulfonic groups; α-groups are easier to eliminate, except that in the 2-naphthol-3-sulfonic acid derivatives the 3-sulfonic group is preferentially eliminated. Among other properties and reactions which are utilized for identification are the fluorescence of the sodium salts in aqueous solution, solubility of the sodium salts in alcohol, coloration with ferric chloride, replaceability of sulfonic groups by nitro groups, and the relative ease of bromination, nitrosation and coupling with diazonium salts. An α-naphthol derivative with the 2- or 4-position free and a β-naphthol derivative with the 1-position free form nitroso compounds on treatment with nitrous acid, but only a nitrosonaphthol with the nitroso and hydroxyl groups in vicinal positions gives a green dye with iron salts. Like sulfonic acids in general, the naphtholsulfonic acids can be characterized as the arylamine salts[456] or as the sulfonyl chlorides prepared by means of phosphorus pentachloride or chlorosulfonic acid.[457]

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[450] Kawaguchi, *J. Soc. Chem. Ind. Japan*, **6**, 1233 (1923).

[451] *BIOS* **1016.**

[452] Vorontsov and Sokolova, *Anilinokrasochnaya Prom.* **5**, 334 (1935); Vorontsov, *J. Applied Chem.* (*U.S.S.R.*) **20**, 464 (1947).

[453] Smith, *JCS* **89**, 1509 (1906); MLB, DRP 36,491.

[454] Forrester and Bain, *J. Soc. Chem. Ind.* **49**, 410T (1930).

[455] Vorontsov and Sokolova, *Prom. Org. Khim.* **3**, 289 (1937).

DIHYDROXYNAPHTHALENES AND THEIR SULFONIC ACIDS

Among the ten possible and known dihydroxynaphthalenes and their numerous sulfonic acids, a few are used as dye intermediates. The important ones are 1,5- and 2,7-dihydroxynaphthalene and the mono and disulfonic acids of 1,8-dihydroxynaphthalene. 1,3-Dihydroxynaphthalene (Naphthoresorcinol) (m.p. 124°) is a reagent for testing glucuronates in urine (Tollens), yields yellow azo dyes, and breaks down to o-toluic acid on fusion with 60% caustic soda at 200°. It can be obtained by several methods, such as the reaction of 3-amino-1-naphthol-5-sulfonic acid with dilute sulfuric acid at 120° or cyclization and decarboxylation of the condensation product of phenylacetyl chloride and sodio-malonic ester.[458] 1,4-Dihydroxynaphthalene (m.p. 176°), like hydroquinone, is prepared by reduction of 1,4-naphthoquinone with sodium hydrosulfite. Methylation with about ten times its weight of 20% methanolic hydrochloric acid at 25° gives 4-methoxy-1-naphthol (m.p. 131°).[9] 1,5-Dihydroxynaphthalene (m.p. 265°) is prepared by the alkali fusion of naphthalene-1,5-disulfonic acid, and is an intermediate for the largely used mordant dye Diamond Black PV. 1,6-Dihydroxynaphthalene (m.p. 137–138°) is similarly prepared from the corresponding disulfonic acid. Alkali fusion of Schaeffer salt gives 2,6-dihydroxynaphthalene (m.p. 218°) in about 50% yield.[458a] 2,7-Dihydroxynaphthalene (m.p. 190°), also prepared similarly but with careful exclusion of air during the alkali fusion,[459] is useful for the preparation of azo and nitroso dyes. Alkali fusion of Crocein acid gives 1,7-dihydroxynaphthalene (m.p. 178°). Azo dyes prepared from 1,7-dihydroxynaphthalene-4-sulfonic acid and its 2-carboxylic acid have now become obsolete. 1,6-Dihydroxynaphthalene-3-sulfonic acid (dioxy-J-acid) and 1,7-dihydroxynaphthalene-3-sulfonic acid (dioxy-G-acid) are prepared by the alkali fusion of 2-naphthol-5,7-disulfonic acid at 175° and of G-acid at 230–240°, respectively.[9] 1,8-Dihydroxynaphthalene 4-sulfonic acid (dioxy-S-acid) can be prepared by either of the indicated methods. The important intermediate, chromotropic acid, is prepared by the action of alkali on the 3,6,8-trisulfonic acid of α-naphthylamine or of α-naphthol; the first process is cheaper, but the second gives a purer product. Chromotropic acid is valuable for the preparation of mordant azo dyes of the afterchrome class and of blue direct cotton dyes capable of forming copper complexes. Chromotropic acid gives a purple color with formaldehyde in presence of sulfuric acid, and the reaction has been used for the spectrophotometric analysis of formaldehyde in small concentrations.[460] Diacetyl can be estimated similarly.[461] 1,8-Dihydroxynaphthalene itself can be obtained by the alkali fusion of naphthasultone or of 1-naphthol-8-sulfonic acid, but it is not used as a dye intermediate. When R-salt is fused with 50% caustic soda solution (3 parts) at 270° in an open pan for a few hours, and the melt diluted and acidified, 2,3-dihydroxynaphthalene-6-sulfonic acid is obtained in 90–95% yield.[9] 2,3-Dihydroxynaphthalene (m.p. 160–161°), used as a coupler in the manufacture of diazo paper,[141] is obtained by the desulfonation of the 6-sulfonic acid. It can couple with one or two moles of a diazonium salt, and it forms two series of coordination compounds, violet and red, with ferric salts.[462]

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[456] Forster and Watson, *J. Soc. Chem. Ind.* **46**, 224T (1927).

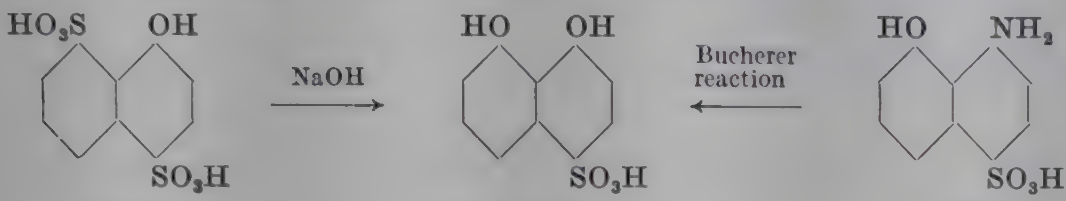
[457] Gebauer-Fuelnegg *et al.*, *JACS* **53**, 2648 (1931).

[458] Metzner, *Ann.* **298**, 388 (1897).

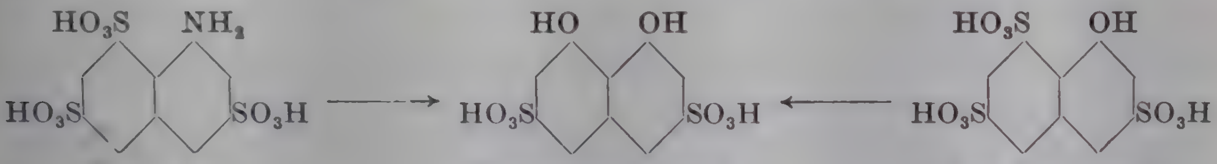
[9] See p. 50.

[458a] For the use of mono-ethers of 2,6-dihydroxynaphthalene as intermediates for metallizable azo dyes, see Ciba, USP 2,452,171.

[459] Ruggli and Courtin, *Helv. Chim. Acta* **15**, 110 (1932).



δ-Acid Dioxy-S-acid S-Acid



Koch acid Chromotropic acid Oxy-Koch acid

In addition to the usual derivatives, many dihydroxynapthalenes form molecular compounds with amines.[463, 464]

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[9] See p. 50.

[460] Bricker and Johnson, *Ind. Eng. Chem. Anal. Ed.* **17,** 400 (1945).

[461] Speck, *Anal. Chem.* **20,** 647 (1948).

[141] See p. 88.

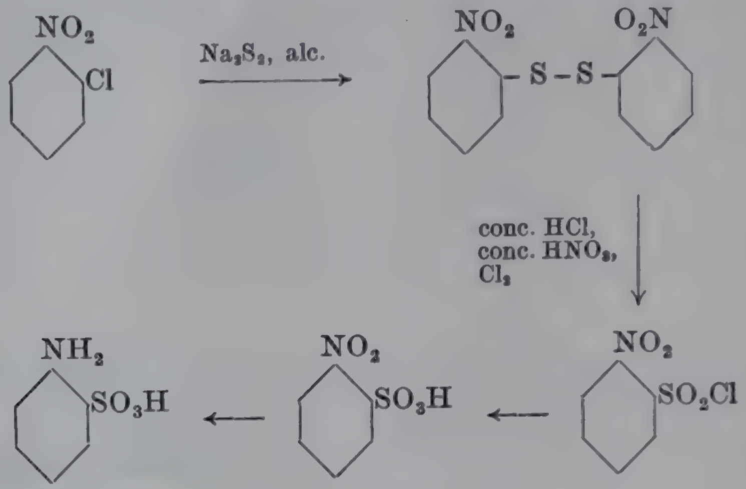
[462] Weinland and Seuffert, *Arch. Pharm.* **266,** 455 (1928).

[463] Kremann, Hemmelmayer, and Riemer, *Monatsh.* **43,** 164 (1922).

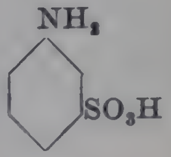
[464] Briner and Kuhn, *Helv. Chim. Acta* **12,** 1075 (1929).

NITROBENZENE- AND ANILINE-SULFONIC ACIDS

Orthanilic acid has limited use as a dye intermediate, and it is prepared from *o*-chloronitrobenzene by the indicated series of reactions.[10, 465] Metanilic and sulfanilic acids are important intermediates for azo dyes.

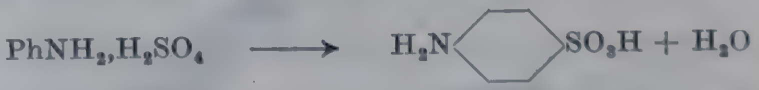


Orthanilic acid



Metanilic acid

Metanilic acid is made by iron reduction of the corresponding nitro compound. Like other substitutions in nitrobenzene, sulfonation requires vigorous conditions, and by heating with 40–45% oleum at 100° or 65% oleum at 80–95° for about 10 hours *m*-nitrobenzenesulfonic acid is obtained, together with traces of the *o*- and *p*-isomers. The sulfonation mixture is neutralized with chalk, gypsum is filtered off, and the filtrate acidified with hydrochloric acid and reduced at the boil with iron. After cooling and adding caustic soda, iron oxide is removed, and the solution of sodium metanilate can be used directly (or after concentration) for diazotization. Phenol-*m*-sulfonic acid is obtained in 90% yield from metanilic acid by diazotization and hydrolysis of a solution of the diazonium salt in 10% sulfuric acid.[10] Sulfanilic acid is manufactured by heating (or "baking") aniline sulfate at 200–220°. Aniline and 98% sulfuric acid are mixe together at about 150°, and the baking is usually carried out in a rotar baker in which the steam evolved can be vented through a hollow axle The end of the reaction is indicated by aniline not being obtained when sample is made alkaline. The crude product (98–99% yield) is purifie by solution in aqueous caustic soda and crystallization of the sodium sal or of the sulfanilic acid obtained by acidification. Sulfonation of sulfanil acid with 20% oleum at 130° for a few hours gives aniline-2,4-disulfonic aci



Sulfanilic acid

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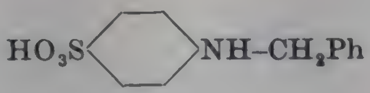
[10] See p. 50.

[465] Wertheim, *OSCV* II, p. 471; Bogert and Stull, *ibid.* I, p. 220.

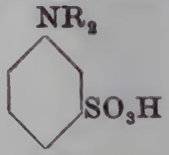
An interesting method of simultaneous amination and sulfonation is to heat an aromatic compound (e.g., benzene, anthraquinone, dibenzanthrone) with sulfuric acid and nitromethane at 140–185° in presence of iron or vanadium salts. Thus benzene gives a mixture of sulfanilic, metanilic, and benzenesulfonic acids.[466]

***N*-Benzylsulfanilic acid** (I), prepared by condensation of sulfanilic acid with benzyl chloride in presence of sodium carbonate at about 95° and then acidification, is an intermediate for acid triphenylmethane dyes. The monosulfonic acid obtained by the sulfonation of *N*-benzyl-*N*-ethyl-*m*-toluidine is used for a similar purpose.

Sulfonation of dimethylaniline and diethylaniline with oleum gives the *m*-sulfonic acids (II) (60%, together with 40% of the *p*-);[466a] (II) can also be prepared by heating metanilic acid with the alkyl chloride and caustic soda solution at 100–150° in an autoclave. Sulfonation of *N*-ethyl-*o*-toluidine below 30°, first with 24% oleum and then with 65% oleum, gives the 4-sulfonic acid (III). The acids (II) and (III) are used for conversion into the corresponding *m*-alkylaminophenols.



(I)



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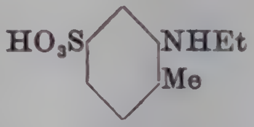
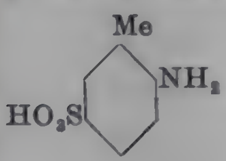


(III)

o-Toluidine-5-sulfonic acid (IV) and *m*-toluidine-6-sulfonic acid (V), like sulfanilic acid, are prepared from *o*- and *m*-toluidine by the baking process; but since they are made on a much smaller scale, the dry acid sulfates are heated in trays at 225–255° in a static baker.[467] When the acid sulfate of *p*-toluidine is heated at 195°, the product is *p*-toluidine-3-sulfonic acid (VI); and *p*-toluidine-2-sulfonic acid (VII) is obtained by reduction of *p*-nitrotoluene-2-sulfonic acid, which is an important intermediate used in making stilbene dyes and is manufactured from *p*-nitrotoluene by sulfonation with oleum. 2-Nitrotoluene-4-sulfonic acid can be obtained in 82% yield by successive sulfonation and nitration of toluene. *m*-4-Xylidine-5-sulfonic acid (VIII) is obtained by baking the acid sulfate of *m*-4-xylidine at 300° for several hours.



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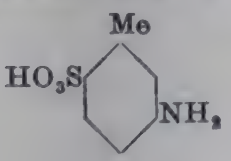

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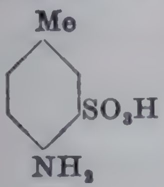

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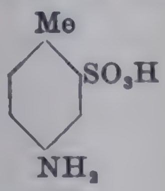

(VII)

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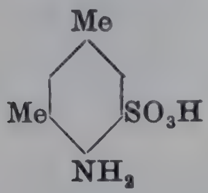
[466] Turski, BP 564,610.

[466a] See also Kurakin, *J. Gen. Chem. U.S.S.R.* **18**, 2089 (1948).

[467] For the preparation of o-toluidine-6-sulfonic acid, see Allen and Van Allan, *Org. Syntheses* **27**, 88 (1947).

4-Nitroaniline-2-sulfonic acid (IX) is prepared in 96% yield from 4-chloronitrobenzene-3-sulfonic acid by treatment with 25% ammonia at 120° and 6 atm. pressure for 30 hours.[10] The usual iron reduction gives *p*-phenylenediaminesulfonic acid, and when the aqueous solution thus obtained is treated with soda ash and then with acetic anhydride below 25°, the product is *p*-aminoacetanilide-3-sulfonic acid (X). 6-Acetamido-*m*-anisidine-4-sulfonic acid (XI) is similarly prepared from 5-nitro-*o*-anisidine-4-sulfonic acid.



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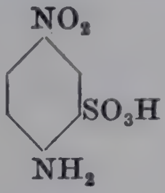

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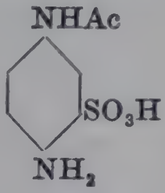

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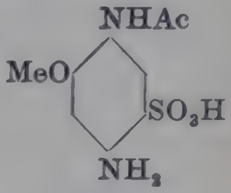

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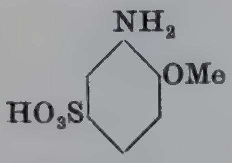

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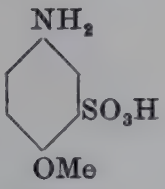

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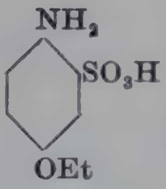

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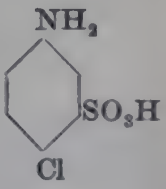
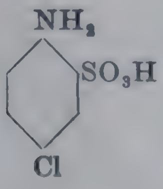


(XV)

Sulfonation[10] of *o*-anisidine with four times its weight of 98% sulfuric acid at 55°, until a sample diluted with water and then alkalized gives a clear solution with no oily drops, yields *o*-anisidine-4-sulfonic acid (XII). When *p*-anisidine is dissolved in 98% sulfuric acid (2 parts) and 26% oleum (1 part) at 30° and treated with 65% oleum (1 part) until sulfonation is complete, the product is *p*-anisidine-2-sulfonic acid (XIII). *p*-Phenetidine-3-sulfonic acid (XIV) is obtained by heating *p*-phenetidine with sodium sulfate (1 part) and 96% sulfuric acid (0.75 part) in *o*-dichlorobenzene, first at 160° under reduced pressure to eliminate water and then at 175° for 18 hours. Sulfonation of *p*-chloronitrobenzene by dissolving it in 24% oleum (2 parts), adding 65% oleum (0.4 part) at 60°, and heating carefully at 100–125° till sulfonation is complete, gives 4-chloronitrobenzene-3-sulfonic acid, from which 4-chloroaniline-3-sulfonic acid (XV) is obtained by reduction with iron and hydrochloric acid. 4-Chloroaniline-2 sulfonic acid (XVI) is prepared by the baking process from the acid sulfat



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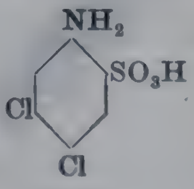
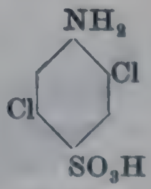
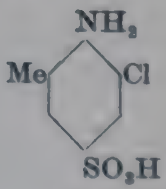


(XVII)



(XVIII)



(XIX)

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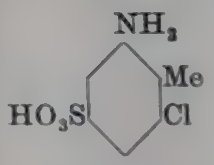
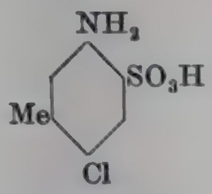
[10] See p. 50.

of *p*-chloroaniline. 3,4-Dichloroaniline-6-sulfonic acid (XVII) and 2,5-dichloroaniline-4-sulfonic acid (XVIII) are obtained by sulfonation of the corresponding dichloroaniline.

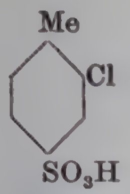
3-Chloro-*o*-toluidine, a by-product in the manufacture of Fast Red TR Base, has found use as the 5-sulfonic acid (XIX), obtained by sulfonation with monohydrate in *o*-dichlorobenzene solution; (XIX) is an intermediate for pyrazolone dyes. Sulfonation of 6-chloro-2-nitrotoluene with 20% oleum at 85° gives the 4-sulfonic acid, which is reduced with iron to 6-chloro-*o*-toluidine-4-sulfonic acid (XX).[6] 6-Chloro-*m*-toluidine-4-sulfonic acid (XXI, C- or CLT-acid) is an important intermediate for azo dyes and lake pigments. It is prepared by sulfonation of toluene with monohydrate at 90–118°, reaction with chlorine in the presence of a little ferric chloride to obtain (XXII), nitration with 74% nitric acid, separation of the required chloronitro acid by the addition of brine, and reduction with iron and acetic acid.[6] Another intermediate for azo color lakes, 2-chloro-5-amino-4-sulfobenzoic acid (XXIII), is obtained by oxidation of (XXII) to the corresponding benzoic acid by permanganate, nitration with 74% nitric acid in monohydrate, and final reduction. When 2-chloro-*p*-toluidine, obtained by iron reduction of 2-chloro-4-nitrotoluene, is sulfonated by the baking process, the product is 2-chloro-*p*-toluidine-5-sulfonic acid (XXIV).



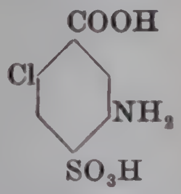
(XX)



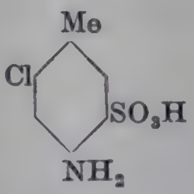
(XXI)



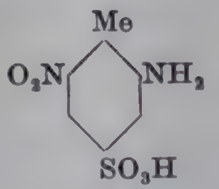
(XXII)



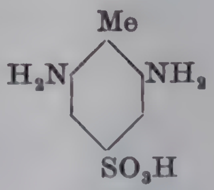
(XXIII)



(XXIV)



(XXV)



(XXVI)

Sulfonation of *o*-nitrotoluene with 26% oleum at 50–80° and then nitration by the addition of sodium nitrate to the sulfonation mixture gives 2,6-dinitrotoluene-4-sulfonic acid, precipitated by the addition of sodium sulfate. Reduction of this dinitro compound with sodium hydrogen sulfide in presence of magnesium oxide gives 6-nitro-*o*-toluidine-4-sulfonic acid (XXV), and iron-acid reduction gives 2,6-diaminotoluene-4-sulfonic acid (XXVI). Dinitration of chlorobenzene-*p*-sulfonic acid followed by iron-hydrochloric acid reduction yields 2,6-diaminochlorobenzene-4-sulfonic acid

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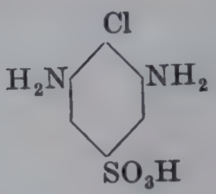
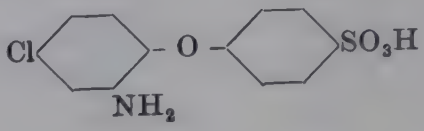
[6] See p. 50.

(XXVII). Sulfonation of 4-chloro-2-aminodiphenyl ether (Fast Red FG Base)[129] with concentrated sulfuric acid at 65° gives the 4′-sulfonic acid (XXVIII).

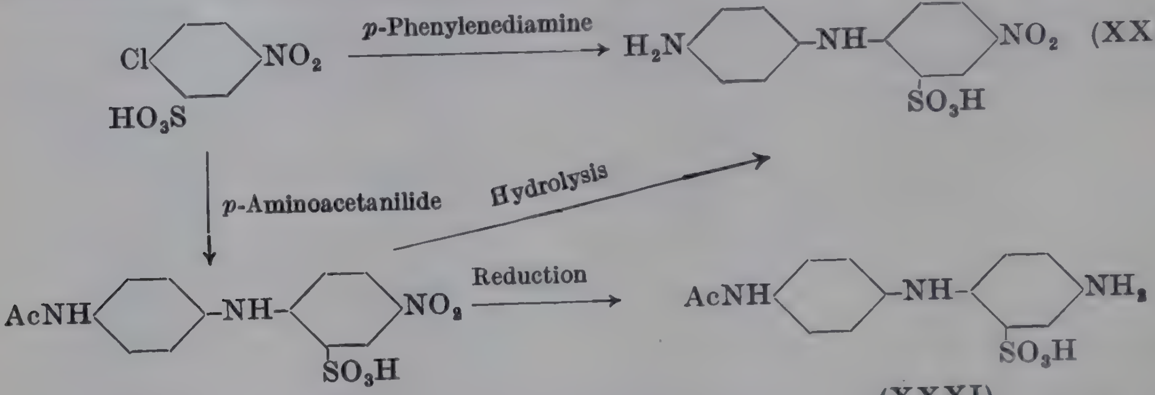
(XXVII)





(XXVIII)

4-Nitro-4′-aminodiphenylamine-2-sulfonic acid (XXIX) is an intermediate used extensively in the manufacture of leather dyes. It is prepared by condensation of *p*-phenylenediamine with one mole of 4-chloronitrobenzene-3-sulfonic acid in boiling aqueous solution in presence of chalk; another route uses *p*-aminoacetanilide and hydrolysis of the acetyl group in the product (XXX). Reduction of (XXX) gives (XXXI), a minor intermediate.

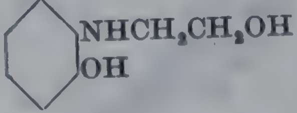


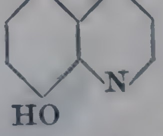
(XXIX) (XXX) (XXXI)

AMINOPHENOLS AND AMINOPHENOLSULFONIC ACIDS

o-Aminophenol (m.p. 174°) is obtained by the reduction of *o*-nitrophenol with sodium sulfide or catalytically with hydrogen, and its derivatives are important for the preparation of mordant azo dyes.[298] Condensation of *o*-aminophenol with ethylene oxide gives (I, Atomal, IG), a useful photographic developer.[239] *o*-Aminophenol is also used to make 8-hydroxyquinoline (II; "oxine") by the Skraup reaction; (II) can be used as an intermediate for mordant azo dyes; it is used in analytical chemistry for the detection and separation of metals, such as aluminium, magnesium and zinc, with which it forms insoluble complexes; and the copper compoun

(I)





(II)

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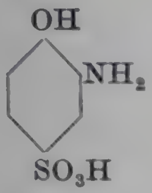
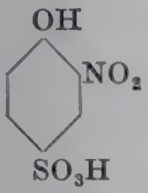
[129] See p. 83.
[298] See p. 129.
[239] See p. 114.

is a fungicide, which on account of its mildew-resisting properties and nontoxic character is a valuable preservative for textiles, leather, and other materials.[468] 7-Iodo derivatives of (II), in which the 5-position is substituted by SO_3H (Chiniofon), Cl (Vioform), or I (Diiodoquin), are useful remedies in amebic dysentery.

The characteristic property of forming "lakes" with metallic salts is due to the vicinal hydroxyl and azo groups in the azo dyes prepared from diazotized *o*-aminophenols. Especially important are the aminophenolsulfonic acids,[469] e.g., (III). Sulfonation of phenol at room temperature gives a mixture of the *o*- and *p*-sulfonic acids with the former as the major product, but above 100° the *p*-compound is almost solely formed. This is not separated, but nitrated and finally reduced to (III). An alternative route to 2-nitrophenol-4-sulfonic acid (IV) is the hydrolysis of 2-chloronitrobenzene-5-sulfonic acid (V) with an equal weight of boiling 30% caustic soda solution for a few hours; (V) is obtained by sulfonating chlorobenzene with monohydrate at 100° and nitrating the sulfonic acid, without isolation and after cooling to 20°, with 67% nitric acid.



(III)



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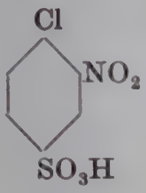
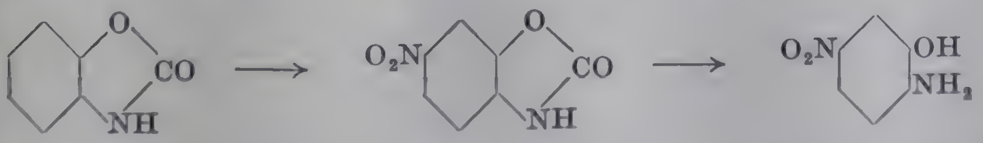


(V)

4-Nitro-2-aminophenol (m.p. 143°) is obtained[470] in about 65% yield by reduction of 2,4-dinitrophenol with aqueous sodium sulfide in presence of ammonia and ammonium chloride at 85°. *o*-Aminophenol condenses with phosgene to form benzoxazolone (VI); nitration of (VI) with mixed acid and fission of the oxazolone ring by hydrolysis with alkali yields 5-nitro-2-aminophenol (VII) as the major product (60%), together with the 4-nitro isomer (10%).[163] Another useful intermediate for mordant

(VI)



(VII)

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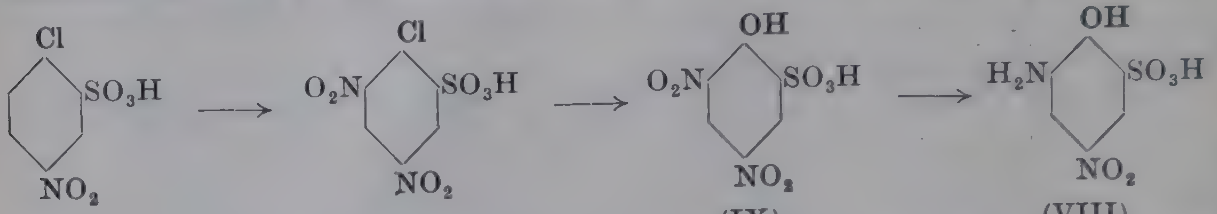
[468] Benignus, *Ind. Eng. Chem.* **40,** 1426 (1948).

[469] Beech, *JCS* 212 (**1948**), has described the preparation of numerous nuclear-substituted *o*-aminophenolsulfonic acids of possible importance as diazonium components in the preparation of metallizable azo dyes.

[470] Laurent and Gerhardt, *Ann.* **75,** 68 (1850); Hertmann and Sillowy, *Org. Syntheses* **25,** 5 (1945).

[163] See p. **94.**

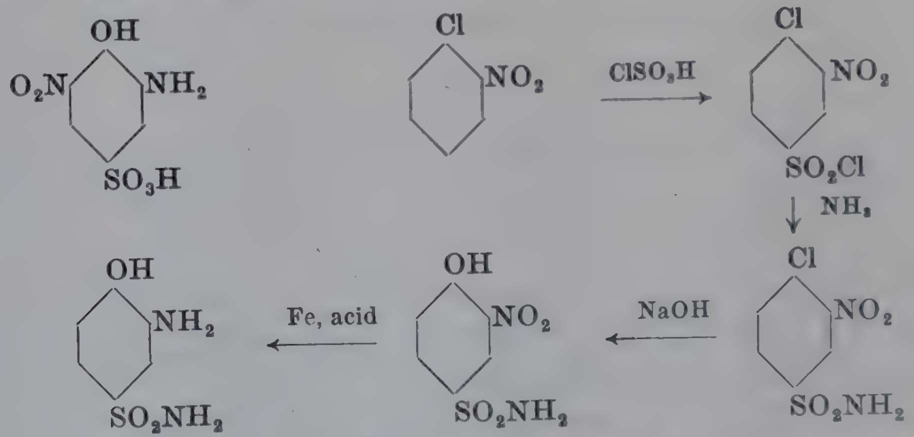
azo dyes is 4-nitro-2-aminophenol-6-sulfonic acid (VIII), prepared by hydrolysis of 1-chloro-2,4-dinitrobenzene-6-sulfonic acid with caustic soda solution to form (IX), which is then reduced with sodium hydrosulfide.[10]


(IX) (VIII)

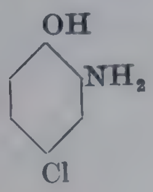
The isomeric 6-nitro-2-aminophenol-4-sulfonic acid (X) is obtained by nitration of (III) in oleum by mixed acid.[3]

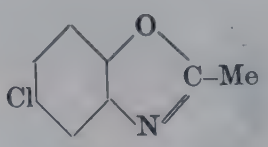
2-Aminophenol-4-sulfonamide (XI) is prepared from *o*-chloronitrobenzene by the indicated series of reactions. The sulfon-*N*-methylamide corresponding to (XI) is prepared similarly.

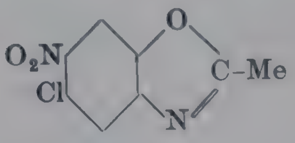
(X)

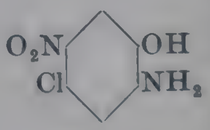

(XI)

4-Chloro-2-aminophenol (XII) is prepared from 2,5-dichloronitrobenzene by heating with 8% caustic soda solution at 130° for 20 hours, and reducing the resultant 4-chloro-2-nitrophenol with iron and sulfuric acid.[10] When (XII) in aqueous suspension is treated with acetic anhydride at 25–30°

(XII)



(XIII)


(XIV)


(XV)

the *N*-acetyl derivative is obtained, which on heating at 185–210° in c dichlorobenzene solution for several hours cyclizes to the oxazole (XIII Nitration of (XIII) gives (XIV), and (XV) is then obtained[10] by fissio of the oxazole ring by heating with 5% caustic soda solution at 70°. Chloro-2-aminophenol-4-sulfonic acid (XVI) is an important intermedi for mordant azo dyes, and is prepared from *o*-chlorophenol by sulfonati nitration of the sulfonic acid without isolation, and final iron reduction.

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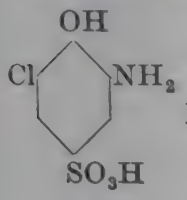
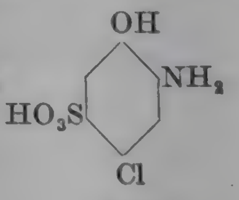
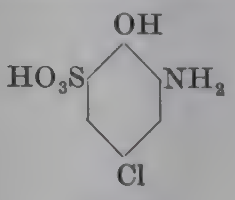
[10] See p. 50.
[3] See p. 50.

Owing to the similarity in the properties of pairs of dyes made by coupling diazotized 4-chloro-2-aminophenol-5- and 6-sulfonic acids (XVII) and (XVIII) with the same coupling component, the identity of (XVII) has been open to question, but the two acids have now been prepared by unambiguous methods and characterized. The acid (XVII) has been prepared by sulfonating 5-chlorobenzoxazolone and then hydrolyzing the 6-sulfonic acid.[471] 3,4,6-Trichloro-*o*-aminophenol, or a mixture of isomers, is an important intermediate. Tetrachloro-*o*-aminophenol can be prepared by chlorinating the benzoxazolone (XIX) from phosgene and 6-chloro-2-aminophenol, followed by hydrolysis.[472]


(XVI)


(XVII)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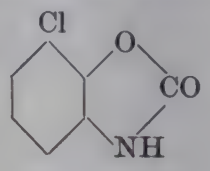
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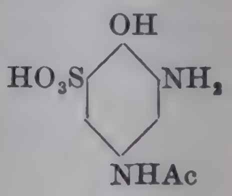
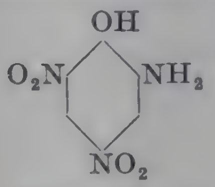
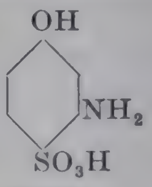

(XX)

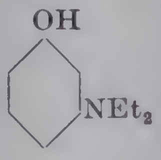
2-Amino-4-acetamidophenol-6-sulfonic acid (XX) is obtained from *p*-acetamidophenol by sulfonation, nitration, and reduction.[10]

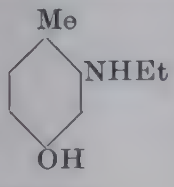
Picramic acid (red needles, m.p. 169°), made by the reduction of picric acid with sodium sulfide or hyposulfite or iron and salt,[473] is stored as an aqueous paste to avoid the danger of explosion. It is an important intermediate for the preparation of the Metachrome or single-bath dyeing type of mordant dye.[298]

***m*-Aminophenol** (m.p. 123°) is prepared by the caustic potash fusion of sodium metanilate at 250°, or by heating resorcinol with aqueous ammonia and ammonium chloride under pressure at 200°. 3-Aminophenol-4-sulfonic acid (XXI) is obtained by heating aniline-2,5-disulfonic acid with twice its weight of 50% aqueous caustic soda at 200° under pressure for 15 hours.[10] *m*-Diethylaminophenol (XXII) and the methyl analog, used in making phthalein dyes of the Rhodamine type, are prepared[6] by heating the corresponding dialkylmetanilic acid with caustic potash at 260–280°.


Picramic acid


(XXI)


(XXII)


(XXIII)

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[471] Guant, Rowe, and Speakman, *J. Soc. Dyers Colourists* **63**, 48 (1947).

[472] IG, BP 443,580; 460,911.

[10] See p. 50.

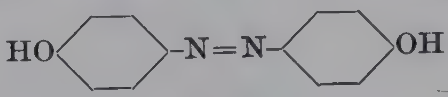
[473] Seyewetz and Blanc, *Chimie & Industrie* **25**, 605 (1930); Clayton, *J. Soc. Dyers Colourists* **46**, 365 (1930); Lyons and Smith, *Ber.* **60**, 181 (1927).

[298] See p. 129.

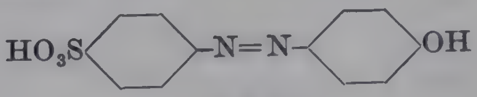
[6] See p. 50.

2-Ethylamino-*p*-cresol (XXIII), also used for phthalein dyes, is prepared[6] by fusion of the corresponding sulfonic acid with a mixture of potassium and sodium hydroxide at 230–240°; purification is effected by vacuum distillation (yield 60%). When *N*-isopropyl-*o*-toluidine is sulfonated with 31.5% oleum at 75°, a mixture of the 4- and 5-sulfonic acids is produced, but on fusion of the mixed sulfonates with caustic potash and soda (13:3) only 2-isopropylamino-*p*-cresol is formed.[474]

***p*-Aminophenol** (colorless plates, m.p. 186°) is valuable as a fur dye, as an intermediate for sulfur dyes, and as a photographic developer. At least four methods of preparation can be used: sulfide reduction of *p*-nitrosophenol; reduction of *p*-nitrophenol by means of iron and acetic acid; electrolytic reduction of nitrobenzene in sulfuric acid solution (Gattermann, 1893);[475] and reduction (hydrosulfite and caustic soda, or Raney nickel) of 4,4′-dihydroxyazobenzene (XXIV), obtained by the alkali fusion of the azo dye (XXV) from diazotized sulfanilic acid and phenol. *p*-Aminophenol is produced in about 40% yield by catalytic reduction of nitrobenzene in 25% sulfuric acid at 110° and 500 lbs. pressure in the presence of platinum oxide or molybdenum sulfide as catalyst.[476] *p*-Aminophenol undergoes ready oxidation to quinone through the unstable *p*-quinonimine. Aminophenols, as well as sensitive amines and phenols, can be stabilized against discoloration by air oxidation by small amounts (less than 0.1%) of hydrazine hydrate[477] or water-soluble mercaptans such as thioglycolic acid.[478] Two *p*-aminophenol derivatives are important photographic developers. *p*-Hydroxyphenylglycine ("photographic glycine," XXVI) is prepared from *p*-aminophenol by condensation with chloroacetic acid in presence of zinc dust and aqueous sodium carbonate and sodium bisulfite at 98–100°. Metol (XXVII) may be prepared by heating hydroquinone with methylamine under pressure or better by decarboxylation of (XXVI), which is effected in a boiling mixture of chlorobenzene and cyclohexanone during 12 hours.[239]



(XXIV)



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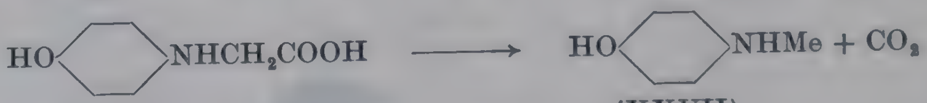

(XXVI) (XXVII)

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[474] National Aniline Co., USP 1,981,515.

[475] Dey, Govindachari, and Rajagopalan, *J. Sci. Ind. Res.* (*India*), **4**, 574 (1946).

[476] Henke, Vaughen, and du Pont, USP 2,198,249.

[477] Dow Chemical Co., USP 1,973,724.

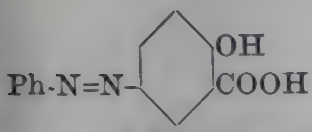
[478] IG, BP 432,480.

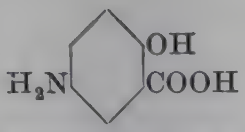
[6] See p. 50.

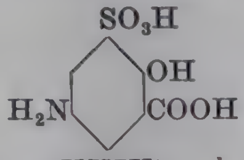
[239] See p. 114.

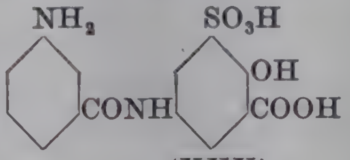
2,4-Diaminophenol, prepared by the iron-hydrochloric acid reduction of 2,4-dinitrophenol, is a photographic developer (amidol).

5-Aminosalicylic acid is a largely used intermediate for mordant azo dyes in which the mordant-dyeing property is due to the *o*-hydroxy-carboxylic acid group. It is prepared from salicylic acid by coupling with diazotized aniline and reducing the 5-benzeneazosalicylic acid (XXVIII) thus obtained by means of boiling sodium disulfide solution until no more aniline distils. Sulfonation of 5-aminosalicylic acid with 20% oleum at 110–120° gives 5-amino-3-sulfosalicylic acid (XXIX).[10] Condensation of the sodium salt of (XXIX) with *m*-nitrobenzoyl chloride in presence of sodium acetate, followed by reduction of the nitro group with sodium hydrogen sulfide solution at 80°, gives 5-(3′-amino)benzamido-3-sulfosalicylic acid (XXX).[10]


(XXVIII)

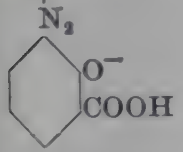

5-Aminosalicylic acid

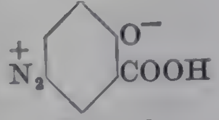

(XXIX)


(XXX)

When salicylic acid suspended in 83% sulfuric acid (5 parts) is treated with 68% nitric acid below 10°, 3- and 5-nitrosalicylic acids are obtained in about equal proportions.[10, 163] The mixture of isomers is reduced by means of iron and aqueous sulfuric acid; the reduction liquor is filtered from the iron sludge, clarified with decolorizing carbon, and treated with sodium nitrite at 10°. Bright yellow crystals of the mixed diazo-oxides (KXXI) and (XXXII) are thus obtained.

Sulfonation of salicylic acid gives the 5-sulfonic acid, from which by nitration and reduction 3-amino-5-sulfosalicylic acid (XXXIII) is obtained.[163] Treatment of (XXXIII) in faintly alkaline solution at 50° with *p*-nitrobenzoyl chloride in presence of sodium acetate, followed by reduction, gives 3-(4′-amino)benzamido-5-sulfosalicylic acid (XXXIV).


(XXXI)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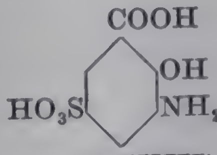
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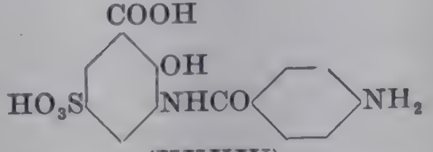
(XXXIV)

4-Aminosalicylic acid, which can be prepared by the carboxylation of *m*-aminophenol or from 4-nitro-*o*-toluidine (Fast Scarlet G Base) through a series of reactions,[479] has been found recently to have considerable use in the chemotherapy of tuberculosis.[480]

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[10] See p. 50.

[163] See p. 94.

[479] Bhate, Panse, and Venkataraman, *Proc. Indian Acad. Sci.* **29 A,** 196 (1949); Sheehan, *JACS* **70,** 1665 (1948); Erlenmeyer *et al., Helv. Chim. Acta* **31,** 988 (1948).

[480] Lehmann, *Lancet* **250,** 15 (1946); Martin *et al., Nature,* **161,** 435 (1948).

NITRONAPHTHOLS AND AMINONAPHTHOLS

All the mononitro-α-naphthols except the 7-nitro compound and all the nitro-β-naphthols except the 3- and 7-nitro compounds have been described;[5] but they have no technical value. 2,4-Dinitro-1-naphthol and its 7-sulfonic acid have interest as acid dyes and as moth-proofing agents.[269] The nitronaphthols are prepared by nitration of naphthols or their derivatives or from the nitronaphthylamines by hydrolysis of the diazonium salts.

Several aminonaphtholsulfonic acids are important intermediates and are considered later, but none of the 14 possible aminonaphthols, all of which are known, is particularly valuable as a dye intermediate, although they have technical possibilities mentioned in patents, and there are one or two instances of their use in the production of commercial dyes. 1-Amino-5-naphthol (Purpurol; m.p. 192°) was a constituent of some blue azo dyes, e.g., Lanacyl Blue BB (C), which are now obsolete. It is now used as an intermediate for sulfur dyes, and is prepared by the alkali fusion of 1-naphthylamine-5-sulfonic (Laurent) acid. 3,7-Dihydroxy-1,2,3,4-tetrahydro(7′,8′-)benzoquinoline, an intermediate for cellulose acetate dyes, is obtained[10] in 52% yield by condensation of 1-amino-5-naphthol with epichlorhydrin in *n*-butanol at 75–114° for about 15 hours in an atmosphere of nitrogen. 1-Amino-7-naphthol (m.p. 205–207°) can be prepared by the alkali fusion of 1-naphthylamine-7-sulfonic acid, first at 265–275° and finally for 5 minutes at 305°. Its *N*-acetyl derivative is a useful azo dye intermediate; its methyl ether gives violet shades when the diazonium salt is used in azoic dyeing.[129] The carbamic esters obtained by condensation of 1-amino-7-naphthol with chloroformic esters can be used for the preparation of azo dyes for wool applicable by the metachrome process.[481] 1-Aroylamido-7-naphthol has been suggested as a coupling component for the production of insoluble azo dyes on the fiber.

1-Amino-2-naphthol, 2-amino-1-naphthol, and 1-amino-4-naphthol have the properties of photographic developers. These aminonaphthols with the amino and hydroxyl groups in the adjacent or *para* positions can be prepared in excellent yield by the reduction of appropriate azo dyes, with use of sodium hydrosulfite and caustic soda for the soluble dyes[482] or of hydrogen in presence of a catalyst such as Raney nickel for dyes that are insoluble in water and soluble in an organic solvent. 1-Amino-2-naphthol can also be conveniently prepared[483] by the hydrosulfite-alkali reduction of 1-nitroso-2-naphthol, which is readily obtained by nitrosation of β-naphthol.[484] As fission products of azo dyes, these aminonaphthols are involved in the determination of the constitution of azo dyes. An interesting reaction by which some of the aminonaphthols can be prepared is the fusion of naphthols and their sulfonic acids with sodamide. The reaction is best carried out in an inert diluent such as naphthalene or quinoline. Thus α- and β-naphthols give the 5-aminonaphthols.[485] In the case of the sulfonic acids the sulfonic group is removed, but the amino group sometimes enters a new position; 1,5-, 1,8- and 2,7-naphtholsulfonic acids give the corresponding aminonaphthols in good yield, but 2-naphthol-6-sulfonic acid (Schaeffer acid) gives 1-amino-6-naphthol. Other routes to the aminonaphthols are partial amination of the dihydroxynaphthalenes by the Bucherer reaction and alkali fusion of naphthylaminesulfonic acids. The latter method is used for instance for the preparation of 1-amino-6- and 7-naphthol,[486] but an interesting exception in this connection is that the alkali fusion of naphthionic acid gives NW-acid and not 1-amino-4-naphthol.

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[5] See p. 50.

[10] See p. 50.

[269] See p, 121

[129] See p. 83

[481] Sandoz, BP 597,542 ; SP 247,598–602.

[482] Conant, Lutz, and Corson, *OSCV* I, p. 49; Fieser, *ibid.* II, p. 39.

[483] Conant and Corson, *ibid.* II, p. 33.

[484] Marvel and Porter, *ibid* I, p. 411.

NAPHTHYLAMINESULFONIC ACIDS AND AMINONAPHTHOLSULFONIC ACIDS

Sulfonic acids of naphthylamines and aminonaphthols are best considered together, the naphthylaminesulfonic acids being intermediates for aminonaphtholsulfonic acids. The aminonaphtholsulfonic acids (e.g., J-, H-, and γ-acids) constitute a group of intermediates of very great importance, since many of the most largely used azo dyes for cellulose and protein fibers are made from them.

α-Naphthylaminesulfonic acids are prepared by (*a*) sulfonation of α-naphthylamine; (*b*) sulfonation and reduction of α-nitronaphthalene; (*c*) nitration and reduction of naphthalenesulfonic acids; (*d*) further sulfonation of the sulfonic acids obtained by methods (*b*) and (*c*); and (*e*) partial desulfonation of the polysulfonic acids obtained by methods (*a*), (*c*), or (*d*). β-Naphthylamine derivatives are prepared by (*a*) the sulfonation of β-naphthylamine or (*b*) the Bucherer reaction on the naphtholsulfonic acids; the second method is inapplicable to 2-naphthol-4-sulfonic acids. The course of sulfonation of the naphthylamines is shown in Charts 10 and 11, but it will be seen later that the sulfonic acids listed in the charts are not all prepared technically by direct sulfonation. In the sulfonation of α-naphthylamine the first sulfonic group enters the 4-, 5-, or 6-position, and the composition depends mainly on the duration of the reaction; by increased time of treatment the main product is that obtained by substitution in the order named. The second sulfonic group never enters the 2-, 3-, or *peri*-position; and the third sulfonic group always enters the 2-position.

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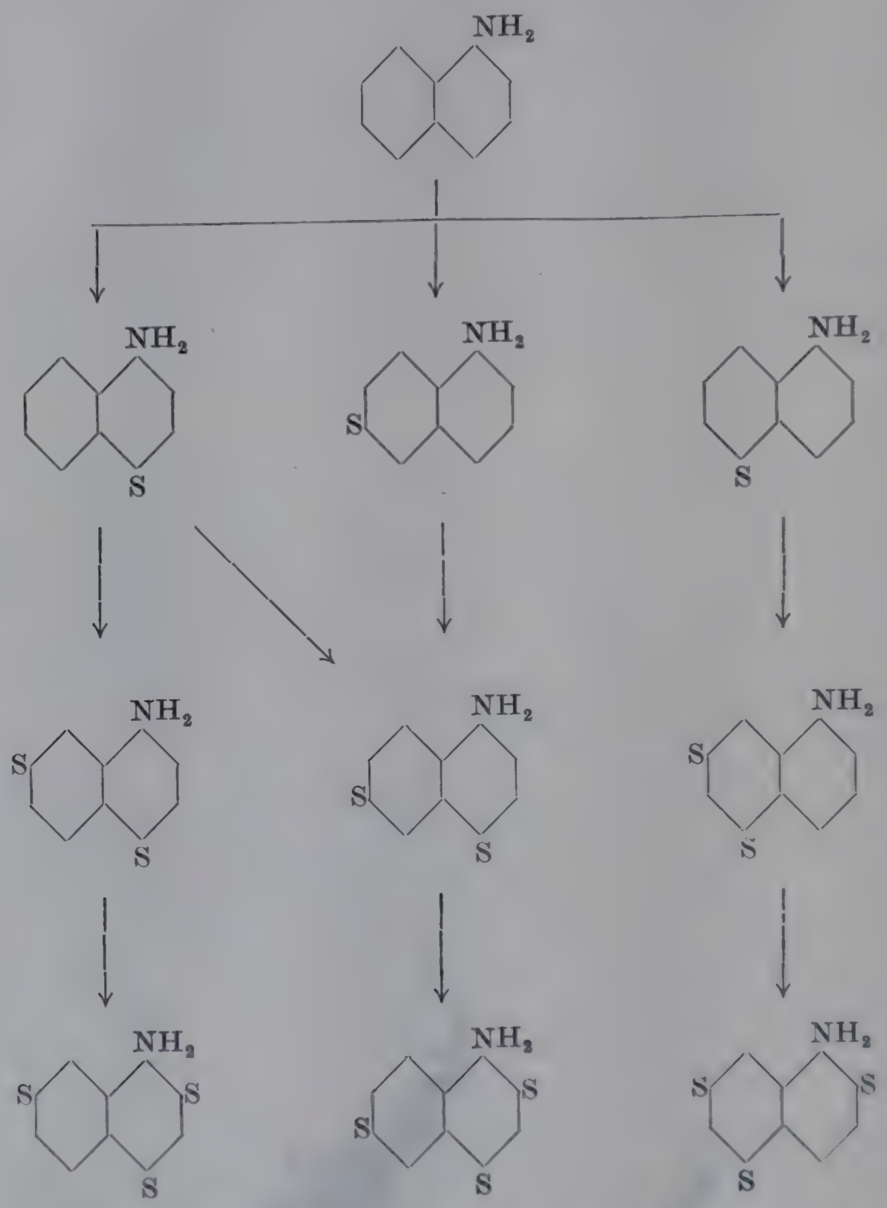
[485] Sachs, DRP 173,522; 181,333; *Ber.* **39**, 3016 (1906).

[486] Brown, Hebden, and Withrow, *JACS* **51**, 1766 (1929).

By direct sulfonation of β-naphthylamine four monosulfonic acids in all of which the sulfonic group enters the unsubstituted ring, six disulfonic acids, and three trisulfonic acids are obtained. Three more trisulfonic

CHART 10

SULFONATION OF α-NAPHTHYLAMINE

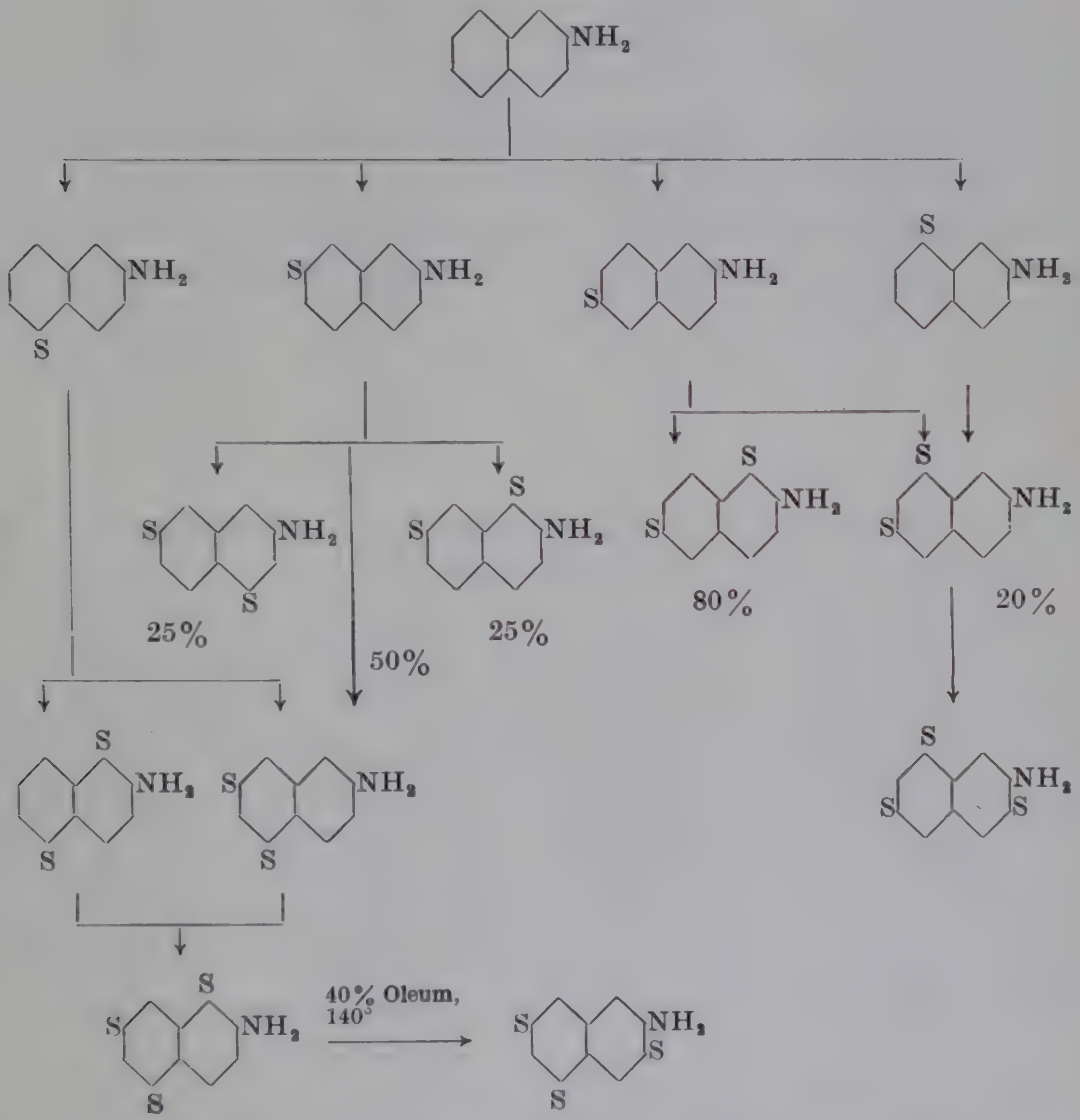


acids can be prepared by sulfonation of β-naphthylamine-3,7- and 4, disulfonic acids, which are not products of the sulfonation of β-naphthylamine but are prepared by other methods.

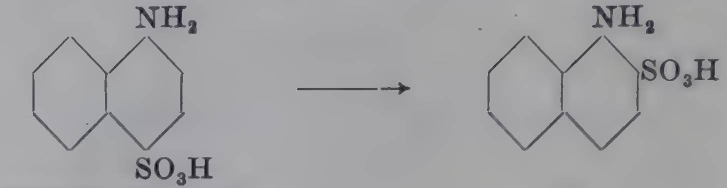
The main method for the preparation of aminonaphtholsulfonic aci is the alkali fusion of naphthylaminesulfonic acids. Sulfonic groups i the 2- and 4-positions in α-naphthylamine and in the 1- and 6-positions i β-naphthylamine are difficult to replace; 5- and 8-sulfonic acids, especiall the latter, are readily replaceable, and in β-naphthylamine the 4-sulfon group can also be replaced. Specific conditions of caustic soda concentration and temperature must be used to avoid replacement of an amino group by hydroxyl, a reaction favored by high temperature and low concentration of alkali. Other routes to aminonaphtholsulfonic acids used in special cases are the reduction of azo- or nitroso-naphtholsulfonic acids (see the preparation of 1-amino-2-naphthol-4-sulfonic acid), and the partial amination of dihydroxynaphthalenesulfonic acids by the Bucherer method (see J-acid derivatives).

CHART 11

SULFONATION OF β-NAPHTHYLAMINE

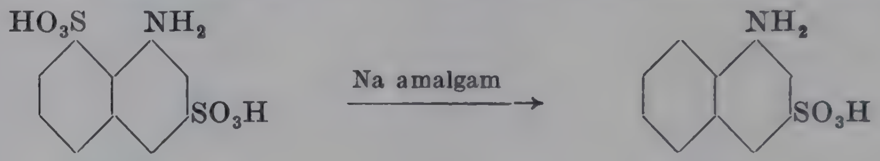


Naphthionic acid, the naphthalene analog of sulfanilic acid, is made similarly from α-naphthylamine sulfate; but the sulfate is mixed with about 3% of oxalic acid to prevent charring, and a somewhat lower temperature of baking (170–180°) is used. It is an important intermediate for azo dyes (e.g., Congo Red and Benzopurpurine). An interesting property is its isomerization to the 2-sulfonic acid (I) by heating at about 200° for a few hours, preferably in admixture with molten naphthalene, or other inert diluent, or *in vacuo*. This method is employed technically for the preparation of (I),[486a] which has a limited use as an intermediate for blue acid dyes of the triphenylmethane series.



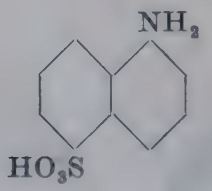
Naphthionic acid (I)

Naphthylamine-3-sulfonic acid (II) is prepared in 95% yield by the action of sodium amalgam at 40-50° on the 3,8-disulfonic acid (III) in aqueous alkaline solution;[9] zinc dust and caustic soda or boiling 75% sulfuric acid can also be used for the desulfonation.

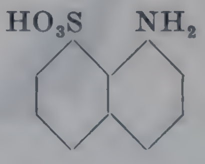


(III) (II)

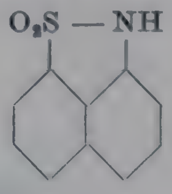
Nitronaphthalenesulfonic acids can be prepared by sulfonation of α-nitronaphthalene or nitration of naphthalenesulfonic acids. When α-nitronaphthalene is sulfonated with 10% oleum at about 90°, the 5-sulfonic acid separates on dilution of the sulfonation mixture with ice (80% yield). The mother liquor contains 1-nitronaphthalene-6- and 7-sulfonic acids. Sulfonation with a mixture of sulfuric and chlorosulfonic acids (or common salt + oleum) results in the nearly pure 5-sulfonic acid. The nitro acid is then reduced to Laurent acid. Nitration and reduction of naphthalene-α-sulfonic acid give a mixture of Laurent acid (about 40%) and peri-acid (about 60%), which may be separated by fractional crystallization of the sodium salts, peri-salt being less soluble. Another method of separation is precipitation of the mixed sodium salts fractionally by means of sulfuric acid, the peri-acid separating first.[487] A reaction of peri-acid which can



Laurent acid



Peri-acid



(IV)

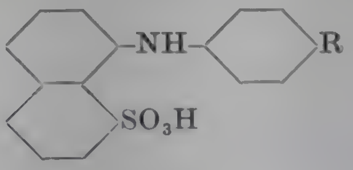
[486a] See also Wintringham *et. al.*, USP 2,479,990.

[9] See p. 50.

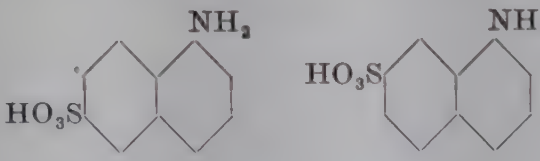
[487] du Pont, USP 1,912,639; Tinker, BP 389,098; National Aniline Co., USP 1,996,822

be used for its estimation is conversion into naphthasultone by diazotizing and boiling the aqueous solution. Another reaction of peri-acid, characteristic also of other α-naphthylaminesulfonic acids in which one sulfonic group is in the 8-position, is dehydration to naphthasultam (IV). Thus peri-acid itself is dehydrated to the parent naphthasultam, m.p. 177-178°, by phosphorus oxychloride ; and naphthasultamsulfonic acids, rather than the naphthylaminesulfonic acids, are sometimes obtained when a peri-acid derivative is prepared by a process involving oleum and a high temperature. The naphthasultams (and their *N*-methyl derivatives) couple with diazonium salts, and naphthasultam simulates in some ways the properties of α-naphthol.[488] The naphthasultams are very stable to alkali, but fission of the sulfonamide link can be effected by means of boiling acids, some desulfonation taking place simultaneously.

N-Phenyl- and tolyl-peri-acids (V; R=H or Me), which are prepared by heating peri-acid with the arylamine and its hydrochloride, or with iodine as catalyst,[489] at about 170°, are useful intermediates for blue azo dyes and green sulfur dyes.



(V)



Cleve acids

Nitration of naphthalene-β-sulfonic acid gives a mixture of 1-nitronaphthalene-6- and 7-sulfonic acids, which are usually not separated but are neutralized with lime and reduced together by iron and a little acetic acid to a mixture of the corresponding amines (Cleve acids). These are important azo dye intermediates, especially as middle components in the preparation of blue trisazo dyes. The pure 1,6- and 1,7-naphthylaminesulfonic acids may be obtained as the sodium salts by fractional salting out, the 7-isomer separating first.[3] Another method of separation is the fractional crystallization of the magnesium salts, the 1,6-salt being less soluble. 1-Naphthylamine-7-sulfonic acid can also be prepared by treatment of 1-naphthylamine-2,7-disulfonic acid with boiling 80% sulfuric acid.

α-Naphthylamine disulfonic acids and aminonaphthol monosulfonic acids. Naphthalene-2,7-disulfonic acid gives Freund acid by nitration and reduction. 1-Naphthylamine-3,7-disulfonic acid (VI) is prepared similarly from naphthalene-2,6-disulfonic acid. Another method used technically is to sulfonate naphthalene to a mixture of the 2,6- and 2,7-disulfonic acids, nitrate and reduce, and finally separate (VI) from Freund acid.[9] 1-Naphthylamine-3,8-disulfonic acid (III) is obtained by nitration and reduction of naphthalene-1,6-disulfonic acid; during the nitration a little 2-nitronaphthalene-4,7-disulfonic acid is also formed, but separation is not necessary, and the product is used directly for conversion into ε-acid by diazotization and boiling with sulfuric acid. When naphthalene-1,5-disulfonic acid is nitrated, the products are 1-nitronaphthalene-4,8-disulfonic acid and (in less amount) 2-nitronaphthalene-4,8-disulfonic acid. Separation can be effected as the sodium or ferrous salts, the salts of the α-nitro compounds being more soluble.[490] The 2-nitro acid is obtained in larger yield by nitration in oleum.[491] Reduction of these two nitronaphthalenedisulfonic acids gives 1-naphthylamine-4,8-disulfonic acid (VII) and 2-naphthylamine-4,8-disulfonic acid respectively. Alkali fusion of (VII) gives S-acid, a useful intermediate for blue and black azo dyes. The prolonged action of 25% oleum at about 30° on naphthionic acid gives 1-naphthylamine-4,6- and 4,7-disulfonic acids (Dahl acids) which are used together as an azo dye intermediate. 1-Naphthylamine-5,7-disulfonic acid (VIII) is prepared by sulfonating Laurent acid with 30–40% oleum at 120° to form the trisulfonic acid (IX), which is then desulfonated to (VIII). Another method for the preparation of (VIII) is the sulfonation of acet-α-naphthalide with 35% oleum, followed by deacetylation. Alkali fusion of (VIII) gives M-acid, useful for making maroon and blue azo dyes. M-Acid can also be prepared by fusing (IX) with alkali to produce 1-amino-5-naphthol-2,7-disulfonic acid, which is then desulfonated to M-acid. 1-Amino-7-naphthol-3-sulfonic acid is prepared[163] by sulfonating 1-amino-7-naphthol with monohydrate at 20–30°.

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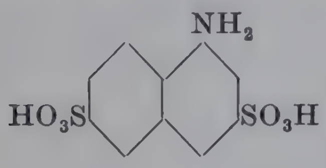
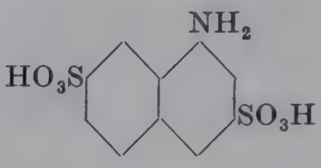
[488] König *et al.*, *Ber.* **55**, 2139 (1922); **57**, 1056 (1924).

[489] Hodgson and Marsden, *J. Soc. Chem. Ind.* **58**, 154T (1939).

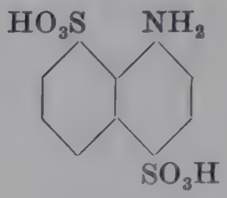
[3] See p. 50.



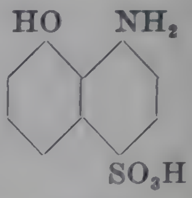
Freund acid



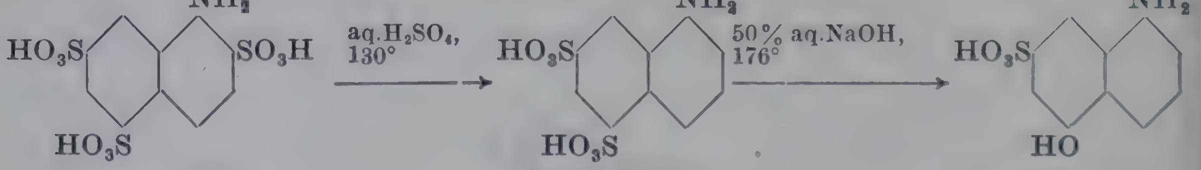
(VI)



(VII)



S-Acid



(IX) (VIII) M-Acid

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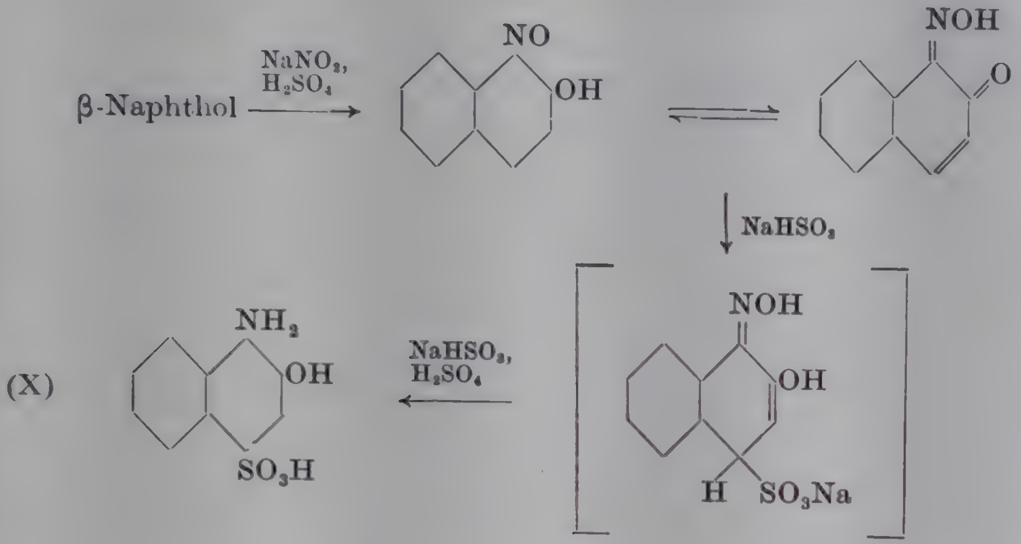
[9] See p. 50.

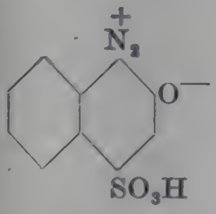
[490] Cassella, DRP 65,997; General Aniline Works, USP 1,968,964.

[491] Montecatini, BP 514,129.

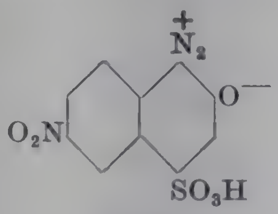
[163] See p. 94.

1-Amino-2-naphthol-4-sulfonic acid (X) is a largely used intermediate for blue-black and black mordant azo dyes. It is obtained in a yield of over 80% by nitrosation of β-naphthol[492] followed by simultaneous reduction and sulfonation of the nitrosonaphthol with sodium bisulfite solution at 20°, after neutralization of excess sulfuric acid with caustic soda.[6, 13, 493] When the reaction mixture is acidified with sulfuric acid and heated to about 50°, the aminonaphtholsulfonic acid (X) separates as a bright grey crystalline substance, which is collected and used for diazotization as a 25% aqueous paste. On diazotization (X) forms the stable diazo oxide (XI),[41, 494] and nitration of (XI) leads to 6-nitro-1-diazo-2-naphthol-4-sulfonic acid (XII),[495] which like (XI) is a valuable intermediate for mordant azo dyes. 1-Amino-2-naphthol-6-sulfonic acid in the form of its methyl and ethyl ethers (XIII) is of great importance for the preparation of blue disazo and trisazo dyes; (XIII) can be prepared by nitrating and reducing 2-ethoxynaphthalene-6-sulfonic acid, obtained by sulfonation of β-naphthyl ethyl ether with chlorosulfonic acid in a suitable solvent. The IG method[9] was to nitrate and reduce β-naphthyl ethyl ether, and sulfonate the amine (XIV). The





(XI)



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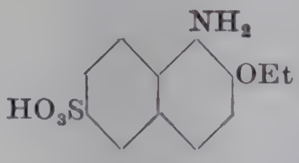
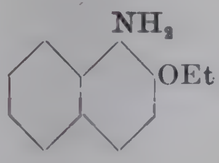


(XIII)



(XIV)

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[492] Fuchs (1875); Marvel and Porter, *OSCV* I, p. 411.

[6] See p. 50.

[13] See p. 50.

[493] Fieser, *ibid* II, p. 42.

[41] See p. 57.

[494] Battegey and Schmidt, *Bull. soc. chim. France* [4] **41**, 205 (1927).

[495] Ruggli *et al.*, *Helv. Chim. Acta* **12**, 1034 (1929).

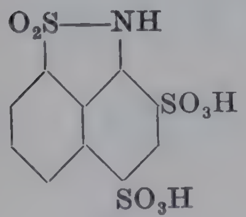
[9] See p. 50.

amine (XIV) can also be obtained by the zinc-acetic acid reduction of 1-benzeneazo-2-naphthyl ethyl ether[496] and by heating 1-chloro-2-ethoxynaphthalene with ammonia under pressure in presence of copper.[497]

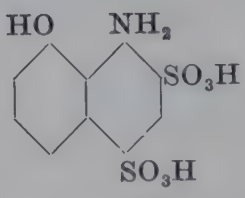
1-Amino-6-naphthol-8-sulfonic acid and 1-amino-7-naphthol-5-sulfonic acid can be prepared by nitration and reduction of an acyl derivative of 2-naphthol-4-sulfonic acid.[498]

1-Naphthylamine trisulfonic acids and aminonaphthol disulfonic acids. 1-Naphthylamine-2,4,7-trisulfonic acid is formed by sulfonating naphthionic acid or 1-naphthylamine-7-sulfonic acid with 40% oleum at 30°. The 2,4,8-trisulfonic acid is unknown, but is obtained in the form of naphthasultam-2,4-disulfonic acid (XV) by sulfonating peri-acid or 1-naphthylamine-4,8-disulfonic acid with oleum at about 90°; alkali fusion of (XV) gives 1-amino-8-naphthol-2,4-disulfonic acid (Chicago acid), which is an intermediate for largely used blue azo dyes for cotton.

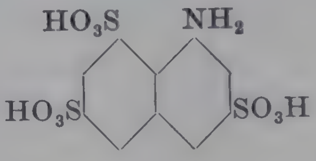
H-Acid. Koch acid (1-naphthylamine-3,6,8-trisulfonic acid), made from the corresponding naphthalenetrisulfonic acid by nitration and reduction, is used for conversion into H-acid. H-Acid is one of the most important dyestuff intermediates; it is used for a wide range of blue, green, and black dyes, and its annual production in the United States is more than four million pounds. On account of the scale of manufacture and the careful control necessary at each stage to obtain maximum yields the entire sequence of operations, starting from naphthalene, is usually carried out in plant set apart for H-acid production. Naphthalene (m.p. 79.8–79.9°, 1000 kg. is trisulfonated by monohydrate (1300 kg.) first at 20°, then at 80–85 for one hour, and finally at 145°; after cooling to 85°, the mixture is dilute with monohydrate (965 kg.), cooled to 40°, and 65% oleum (2560 kg is added during 8 hours. The temperature is raised to 145°, at which it maintained for 2½ hours. After cooling to 60° more 65% oleum (300 kg is added, and the temperature maintained at 150–155° for 2–3 hours. T mixture is cooled to 100°, diluted with water (400 l.) in one hour, a directly nitrated by mixed acid (20% excess of nitric acid) at 35–40° in hours. The solution of 1-nitronaphthalene-3,6,8-trisulfonic acid t



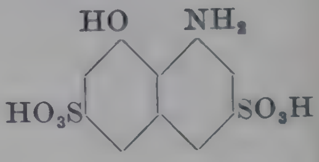
(XV)



Chicago acid



Koch acid



H-Acid

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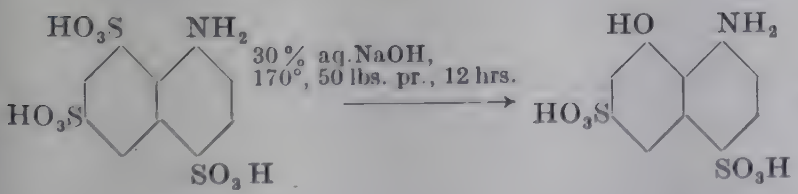
[496] Charrier and Ferreri, *Gazz. chim. ital.* **42,** II, 135 (1912).

[497] Ciba, BP 376,667.

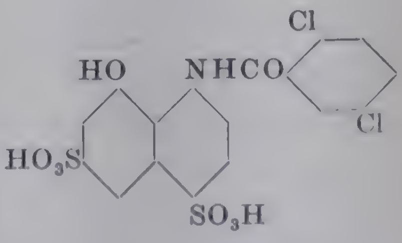
[498] Geigy, SP 220,749; 234,714.

obtained is treated at 60–90° with lime to faint acidity, gypsum filtered off, and reduction to Koch acid carried out by iron powder and water containing a little acetic acid. After the addition of magnesium oxide the iron sludge is filtered off, and Koch acid precipitated as a partly neutralized calcium-sodium salt by the addition of salt and hydrochloric acid; it is then converted into the trisodium salt, which is fused with caustic soda (8 moles as a 23.5% lye) at 178–182° in an autoclave (about 6 atm. pressure) for 6 hours. On filtering and acidifying with sulfuric acid H-acid is obtained in a yield of 85% calculated on Koch acid.[163] An overall yield of 50% from naphthalene is obtainable. It is stated[13] that, in the alkali fusion of Koch acid to H-acid, 2–3% of 1-naphthylamine-6-hydroxy-3,8-disulfonic acid is formed as a by-product; this can be kept to a minimum by control of the quality of the Koch acid as well as of the purity and concentration of the caustic soda, which must be free from chlorate. H-Acid in solution is unstable; it is therefore used directly or dried to a powder for storage. The *N*-acyl (e.g., *N*-acetyl, *N*-benzoyl, *N*-*p*-toluenesulfonyl) derivatives of H-acid are useful intermediates for fast red and violet azo dyes. 1-Chloro-8-naphthol-3,6-disulfonic acid, prepared from H-acid via the diazonium salt, gives bright blue azo dyes.

Nitration and reduction of naphthalene-1,3,5-trisulfonic acid gives 1-naphthylamine-4,6,8-trisulfonic acid (XVI). The conditions of trisulfonation of naphthalene are adjusted so as to produce the maximum amount of the 1,3,5-acid, but the formation of some 1,3,6-acid is unavoidable, so that (XVI) is admixed with Koch acid. Koch acid is separated as the calcium salt, and the filtrate contains the calcium salt of (XVI), which can be salted out as the monosodium salt by means of hydrochloric acid and sodium chloride.[163] Alkali fusion converts (XVI) into K-acid (Kalle acid), which finds considerable use as an azo dye intermediate similar to H-acid. The *N*-acyl derivatives of K-acid (e.g. XVII) yield fast red and violet azo dyes.



(XVI) K-Acid



(XVII)

A notable use for (XVI) is the preparation of Germanin (Bayer 205; Antrypol, ICI), a valuable remedy for African sleeping sickness.

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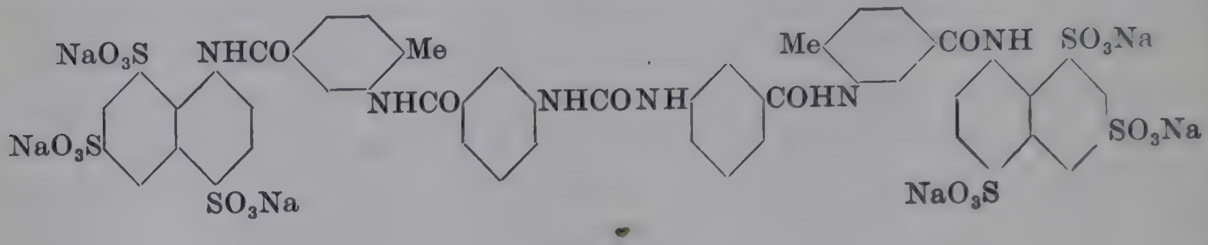
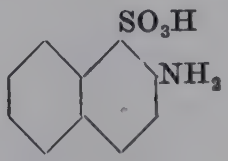
[163] See p. 94.

[13] See p. 50.

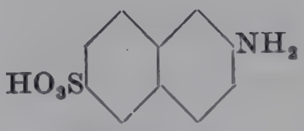
β-Naphthylamine monosulfonic acids. 2-Naphthylamine-1-sulfonic acid (Tobias acid), useful for making azo color lakes, is prepared from 2-naphthol-1-sulfonic acid by the Bucherer reaction. A yield of over 95% is obtainable[6] by heating 2-naphthol-1-sulfonic acid (1.73 parts) with ammonia (0.53 parts as 20% solution) and ammonium sulfite prepared from ammonia (0.27 parts) and sulfur dioxide (0.47 parts) at 150° for 30 hours and 10 atm. pressure; after recovery of ammonia Tobias acid is precipitated by hydrochloric acid. It can also be prepared by sulfonating β-naphthylamine in an inert solvent with chlorosulfonic acid[499] or sulfur trioxide.[500]



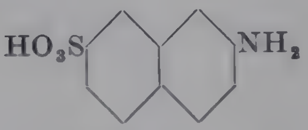
Germanin



Tobias acid



Brönner acid



Cassella acid F

By the monosulfonation of β-naphthylamine with concentrated sulfuric acid below 120°, the 8-sulfonic acid (about 44%) and the 5-sulfonic acid (55%) are formed.[501] They are generally used without separation, which can be effected by means of the solubility of the sodium salt of the 5-acid in alcohol. β-Naphthylamine-4-sulfonic acid, Brönner acid, and Cassella acid F are prepared from the corresponding naphtholsulfonic acids by the Bucherer reaction. A second route to Brönner acid is treatment of β-naphthylamine with thrice its weight of concentrated sulfuric acid at 160–180° for 2 hours, when about equal parts of the 6- and 7-acids are formed; they can be separated by taking advantage of the sparing solubility of the sodium salt of the 6-acid.

β-Naphthylamine disulfonic acids and aminonaphthol monosulfonic acids. 2-Naphthylamine-1,5-, 1,6-, 1,7-, 3,7-, 4,7-, and 4,8-disulfonic acids have little or no technical interest. The 1,5-acid is obtained by sulfonation of the 1- or 5-monosulfonic acid. The 1,6-acid is obtained. together with the 6,8-acid, when the 6-monoacid is sulfonated; or by the

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[6] See p. 50.

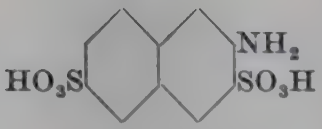
[499] British Dyestuffs Corp., BP 175,019.

[500] du Pont, USP 1,969,189.

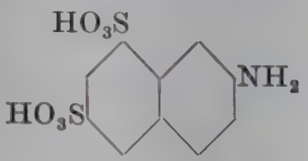
[501] Green and Vakil, *JCS* **113**, 35 (1918).

Bucherer reaction. The 1,7- and 3,7-acids are best prepared by the Bucherer reaction. Of the β-naphthylaminedisulfonic acids only the 4,7- and 4,8-acids are prepared by the reduction of the corresponding nitronaphthalenedisulfonic acids; this in fact is the only route to the 4,8-acid. The requisite nitronaphthalenedisulfonic acids are obtained, together with α-nitro derivatives, when naphthalene-1,6- and 1,5-disulfonic acids are nitrated.

Amido-R-acid (2-naphthylamine-3,6-disulfonic acid) and amido-G-acid (2-naphthylamine-6,8-disulfonic acid) are so called in the dyestuff industry in spite of their being amines and not amides; amino-R-acid would refer to 1-amino-2-naphthol-3,6-disulfonic acid. These acids can be prepared from R-acid and G-acid by the Bucherer reaction. Amido-R-acid is used as a coupling component for a few azo dyes; on fusion with 75% caustic soda at 250° it gives 2-amino-3-naphthol-6-sulfonic acid, which has no technical value. The technical preparation of amido-G-acid involves sulfonation of β-naphthylamine as described later in connection with amido-J-acid.

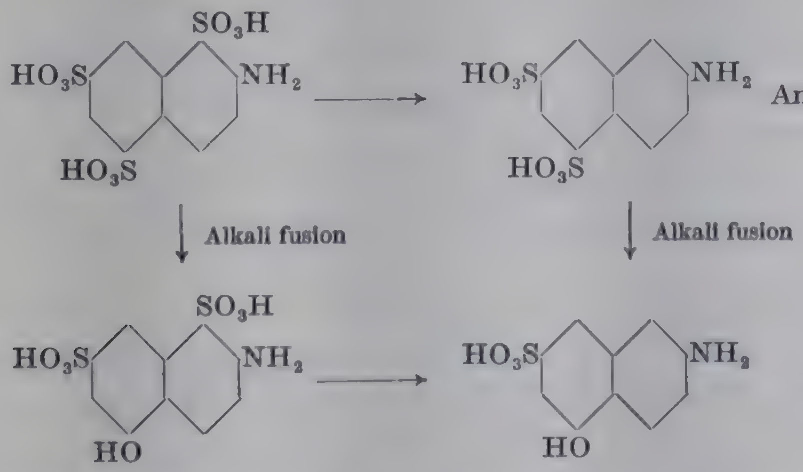


Amido-R-acid



Amido-G-acid

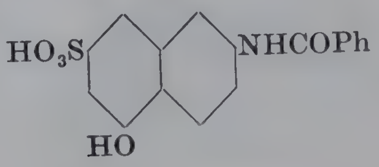
J-Acid and its derivatives. Amido-J-acid is formed when 2-naphthylamine-5- or 7-monosulfonic acid is agitated with oleum for several hours at 25°; but it is best prepared by the desulfonation of 2-naphthylamine-1,5,7-trisulfonic acid (XVIII). By the sulfonation of β-naphthylamine progressively with slightly fuming sulfuric acid at 55° and stronger oleum at 85°, a mixture of (XVIII) and amido-G-acid is obtained, and the latter acid is precipitated (44% yield) on dilution under specified conditions. When the filtrate is boiled, the 1-sulfonic group in (XVIII) is removed as usual, and amido-J-acid results in a yield of 37% calculated on the β-

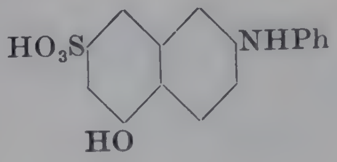


(XVIII) Amido-J-acid
(XIX) J-Acid

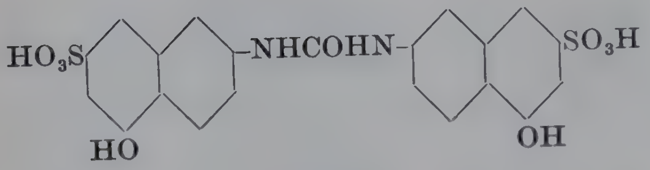
naphthylamine.[502] Alkali fusion then gives J-acid, used in large quantities for the production of direct azo dyes for cotton and other cellulose fibers. A method of preparation of 2-naphthylamine-1,5,7-trisulfonic acid (XVIII), which avoids the use of the toxic β-naphthylamine, is sulfonation of Tobias acid. An alternative route to the important J-acid from (XVIII) is fusion with 65% caustic soda solution at about 220° to produce 2-amino-5-naphthol-1,7-disulfonic acid (XIX), which is then desulfonated to J-acid by boiling aqueous sulfuric acid. *N*-Alkyl- and *N*-aryl-J-acids, *N*-benzoyl-J-acid (XX), the *m*- and *p*-nitro- and aminobenzoyl analogs, and "carbonyl-J-acid" (XXI) are important intermediates. The urea derivative (XXI) is

(XX)

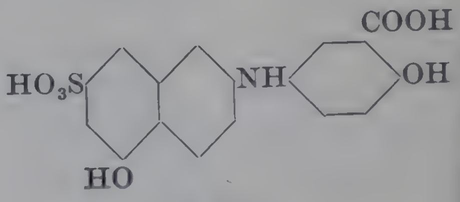




N-Phenyl-J-acid

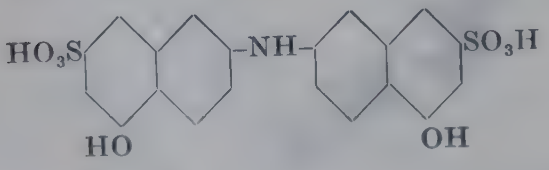


(XXI)

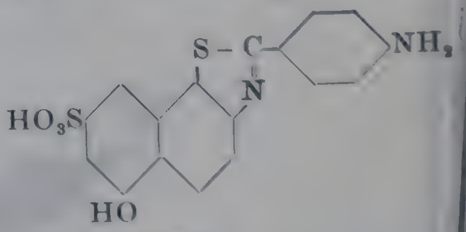


(XXII)

obtained in almost theoretical yield by treating the sodium salt of J-acid in aqueous solution with phosgene in presence of sodium carbonate. Th *N*-alkyl and *N*-aryl compounds are prepared by heating J-acid (or 2,5 dihydroxynaphthalene-7-sulfonic acid) with the appropriate amine an sodium bisulfite under pressure.[9] Thus *N*-phenyl-J-acid is obtained i 85% yield by refluxing molecular proportions of J-acid and aniline wit 6% sodium bisulfite solution and a little soda ash for 40 hours. The salicyl acid derivative (XXII) gives mordant azo dyes. Di-J-acid (XXIII) prepared in 90% yield by heating J-acid with about an equal weight 40% sodium bisulfite solution at 106° for 36 hours. J-Acid and γ-ac (see below) are converted into the corresponding *N*-diguanidino compoun



(XXIII)



(XXIV)

when heated at 100–135° with dicyandiamide in pyridine.[503] Prolo treatment of J-acid with *p*-aminobenzaldehyde and sodium polysu solution ($Na_2S_{1\cdot7}$) at 103° gives the thiazole derivative (XXIV). The *m*-aminophenyl analog is prepared similarly from *m*-nitrobenzaldehyde.[9, 163]

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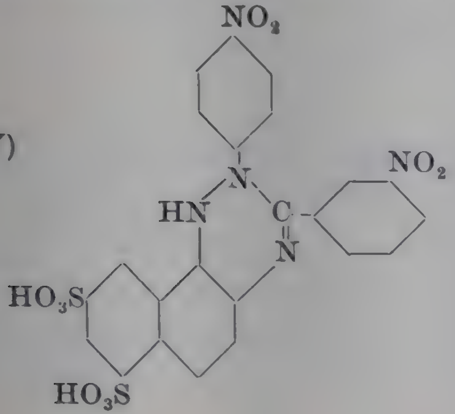
[502] Ofitzerov, *Anilinokrasochnaya Prom.* **4,** 491 (1934).

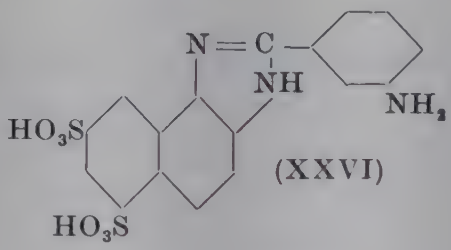
[9] See p. 50.

[503] Jacobs, Jolles, and ICI, BP 585,766.

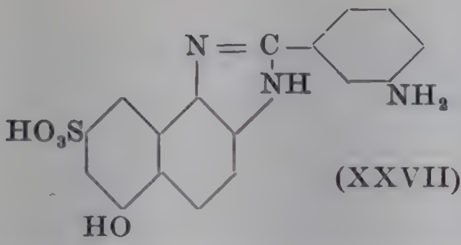
Condensation of *m*-nitrobenzaldehyde with the azo dye obtained by coupling 2-naphthylamine-5,7-disulfonic acid with diazotized *p*-nitroaniline gives the triazine derivative (XXV). Reduction of (XXV) with iron and boiling dilute hydrochloric acid gives the imidazole (XXVI) in 95% yield, and fusion of (XXVI) with 40% potassium hydroxide at 175° finally leads

(XXV)





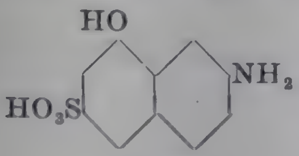
(XXVI)



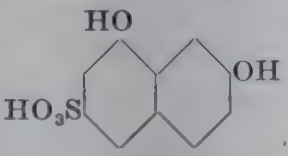
(XXVII)

to 2-(3′-amino)phenyl-6-hydroxynaphthimidazole-8-sulfonic acid (XXVII) in nearly quantitative yield.[9]

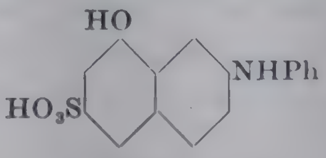
γ-Acid is a very important intermediate for acid azo dyes, being second only to H-acid. γ-Acid is in fact used for a wider variety of purposes than even H-acid, and numerous examples of dyes of different types and



γ-Acid



(XXVIII)



N-Phenyl-γ-acid

dyeing properties made from γ-acid are quoted later. It is used for instance for making black direct cotton dyes. Alkali fusion of amido-G-acid gives γ-acid. *N*-Phenyl-γ-acid, which can be prepared by heating 1,7-dihydroxynaphthalene-3-sulfonic acid (XXVIII) with aniline and aniline salt under pressure, finds use as a component in brown azo dyes for cotton. Other *N*-substituted derivatives of γ-acid (e.g., the *N*-methyl, *N*-β-hydroxyethyl, *N*-*p*-carboxyphenyl, and *N*-acetyl compounds) are also used, but these are much less important than the similar J-acid derivatives.

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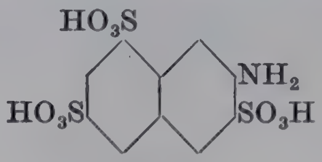
[9] See p. 50.

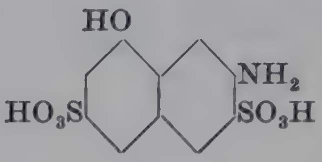
[163] See p. 94.

4-Nitro-2-amino-1-naphthol-6-, 7-, and 8-sulfonic acids have been prepared by reduction of the 2,4-dinitro compounds with sodium sulfide in presence of magnesium chloride.[504]

2-Naphthylamine-3,6,8-trisulfonic acid (XXIX) is prepared by baking the sulfate of amido-G-acid. Alkali fusion of (XXIX) gives 2R-acid,



(XXIX)



2R-Acid

which is used to a limited extent for the preparation of disazo and trisazo dyes.

Few diaminonaphthalenesulfonic acids are now used as dye intermediates. 1,2-Diaminonaphthalene-5-sulfonic acid, prepared by the zinc dust-ammonia reduction of 2-benzeneazo-1-naphthylamine-5-sulfonic acid, and 1,5-diaminonaphthalene-3,7-disulfonic acid, prepared by nitration and reduction of naphthalene-2,6-disulfonic acid, are two intermediates of this type which have limited use.

Characterization of naphthylamine- and aminonaphthol-sulfonic acids. Qualitative tests which are useful for distinction are the fluorescence of aqueous solutions of the sodium salts and the colorations produced by ferric chloride and by hypochlorites. The naphthylaminesulfonic acids do not form salts with the arylamines, but the *N*-acyl (e.g., the *N*-acetyl derivatives) do.[505] The naphthylaminesulfonic acids on reaction with chlorosulfonic acid form the sulfonyl chlorides, from which the anilides can be prepared; thus the anilides of 1-naphthylamine-4-, 5-, 6-, 7- and 8-monosulfonic acids melt at 190°, 171°, 127–128°, 146–147°, and 139–140°.[506] The naphthylaminemonosulfonic acids form with benzoylguanidine colorless salts, which crystallize well and melt sharply.[507]

For purposes of characterization the naphthylaminesulfonic acids may be diazotized and then converted by hydrolysis into the corresponding naphtholsulfonic acids, which are then identified by the methods outlined earlier.

The reactions of desulfonation and hydrolysis, to which references have been made in connection with the preparation of the naphthylamine- and aminonaphthol-sulfonic acids, are obviously of value also in constitutional studies. Thus the positions of the amino and sulfonic groups in 1-naphthylamine-4,6,8-trisulfonic acid follow from the conversions outlined in Chart 12. The replacement of sulfonic groups follows certain general rules. Sulfonic groups in an α-position, and more particularly those in the peri position, are preferentially replaced by hydroxyl during alkali fusion. Acids containing a 3-sulfonic group, by drastic alkali fusion, yield hydroxytoluic acids; 1-naphthylamine-3-sulfonic acid itself on treatment with 60% caustic soda at 280° gives *o*-toluic acid in good yield. Replacement of sulfonic groups by hydrogen also takes place preferentially in α-positions; the peri position is attacked first by alkaline reducing agents (sodium amalgam or zinc and caustic soda), whereas the 4-position is attacked preferentially by boiling dilute sulfuric acid. 1-Naphthylamine-4-sulfonic acids yield 2,4-dibromo-1-naphthylamine derivatives, the 4-sulfonic group being replaced.[508]

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[504] Ciba, BP 487,718.

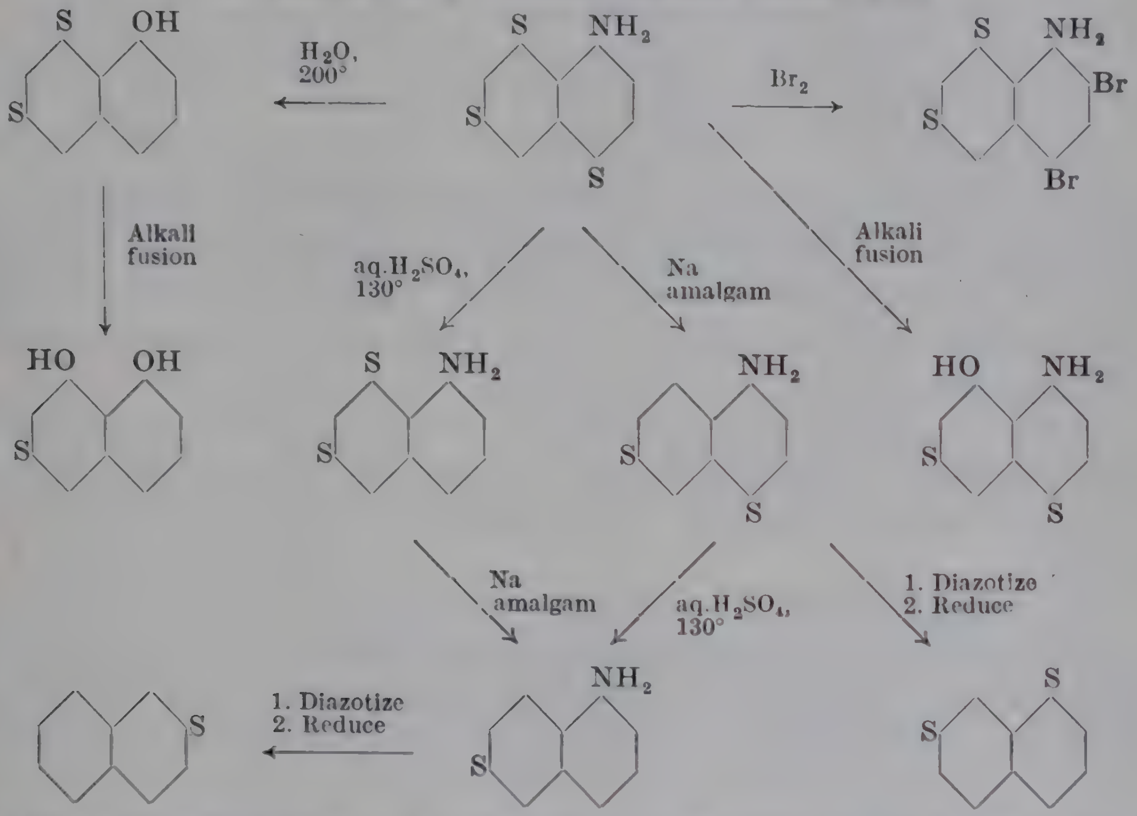
[505] Forster *et al.*, *J. Soc. Chem. Ind.* **46**, 224T (1927); **47**, 155T, 157T (1928).

[506] Heller and Sturm, *J. prakt. Chem.* (ii) **121**, 193 (1929).

[507] Perrot and Barghon, *Compt. rend* **225**, 308 (1947).

CHART 12

CONVERSIONS OF A NAPHTHYLAMINESULFONIC ACID


S
OH
S
H_2O, 200°
S
NH_2
S
S
Br_2
S
NH_2
Br
S
Br
Alkali fusion
aq. H_2SO_4, 130°
Na amalgam
Alkali fusion
HO
OH
S
S
NH_2
S
NH_2
S
S
HO
NH_2
S
S
Na amalgam
aq. H_2SO_4, 130°
1. Diazotize
2. Reduce
S
1. Diazotize
2. Reduce
NH_2
S
S
S

These acids can generally be estimated by titration with diazotized *p*-nitroaniline. The behavior of aminonaphtholsulfonic acids towards diazonium salts under acidic and alkaline conditions of coupling is important in the preparation of azo dyes.[509]

SULFONYL CHLORIDES AND THEIR DERIVATIVES

Benzene- and toluenesulfonyl chlorides have been mentioned earlier. Other examples of sulfonyl chlorides used as dye intermediates are *m*-nitrobenzenesulfonyl chloride (I), 2-nitrotoluene-4-sulfonyl chloride (II), and 4-nitrotoluene-2-sulfonyl chloride (III), which are all prepared[10] by reaction of the nitrohydrocarbon with chlorosulfonic acid (4 moles) at 100° for a few hours and by then drowning the cooled (20°) reaction mixture in ice-water.[509a] *p*-Nitrobenzenesulfonyl chloride can be prepared in high yield from 4,4′-dinitrodiphenyl disulfide by treatment with chlorine in presence of concentrated nitric and hydrochloric acids.[510] 4-Chloronitrobenzene-3-sulfonyl chloride (IV) is prepared by heating the sulfonic acid with chlorosulfonic acid (9.4 moles).

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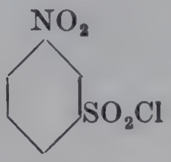
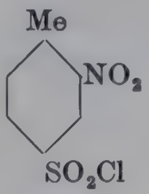
[508] Heller *et al.*, *Angew. Chem.* **43**, 1132 (1930).

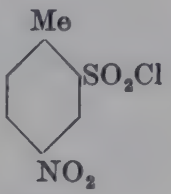
[509] See Chapter XI.



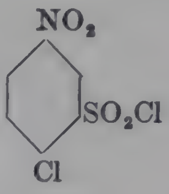
(I)



(II)



(III)

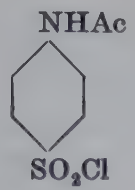


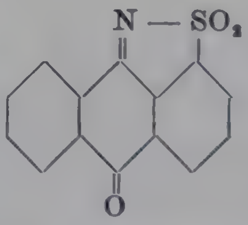
(IV)

p-Acetamidobenzenesulfonyl chloride (V; m.p. 149°) is prepared in large quantities as an intermediate for sulfa drugs. A yield of about 80% is obtained[511] by the action of chlorosulfonic acid (5 moles) on acetanilide at 15°.

Anthraquinonesulfonyl chlorides are obtained by heating the dry sodium sulfonates with phosphorus pentachloride; boiling phosphorus oxychloride is a convenient solvent. The β-compound can also be prepared by heating the β-sulfonic acid with chlorosulfonic acid, but the α-sulfonic acid is unaffected by this treatment. The mono- and disulfonyl chlorides are markedly stable to hydrolysis, being scarcely affected by boiling water after several hours. Whereas the β-sulfonyl chloride (pale yellow plates, m.p. 197°) reacts with ammonia in the normal manner to form the sulfonamide, the α-sulfonyl chloride (pale yellow plates, m.p. 218°) yields the isothiazole derivative (VI).

(V)





(VI)

Sulfonyl chlorides of aromatic amines provide a useful method of building up dye molecules from simpler units, and sulfonyl chlorides of this type can be prepared directly from the aminoanthraquinonesulfonic acids by the action of phosphorus pentachloride, protection of the amino group being unnecessary.[512]

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[10] See p. 50.

[509a] See also British Celanese Co., BP 625,757.

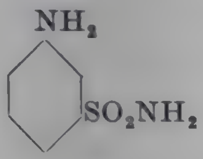
[510] Allied Chemical and Dyestuff, BP 602,597; cf. Wertheim, *OSCV* II, p. 471.

[511] Smiles and Stewart, *ibid.* I, p. 8.

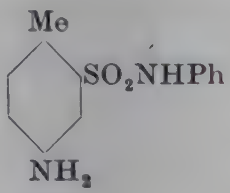
[512] IG, BP 397,190.

Sulfonamide, sulfone, and arylsulfonate groups are useful in azo dyes for the improvement of dyeing and fastness properties.[129, 508] Primary amines containing sulfonamide and sulfone groups are employed from this point of view for diazotization and coupling or for conversion into pyrazolones, which can be coupled with diazonium salts.[513]

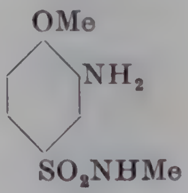
m-Aminobenzenesulfonamide (VII) is prepared by treating (I) in water with 25% ammonia at 50–60°, and reducing the product with iron and hydrochloric acid. The product of the condensation of (I) with aniline in presence of sodium acetate solution and milk of lime, followed by reduction, is *m*-aminobenzenesulfonanilide. *p*-Toluidine-2-sulfonanilide (VIII) is prepared similarly from (III). For the preparation of *o*-anisidine-4-sulfonmethylamide (IX), acet-*o*-anisidide is condensed with chlorosulfonic acid, the sulfonyl chloride (X) condensed with 25% aqueous methylamine at 25° and the acetyl group hydrolyzed by boiling water containing about 30% hydrochloric acid and 12% sulfuric acid until a clear solution is obtained. On replacement of methylamine by diethylamine and dibutylamine, respectively, the products are Fast Red ITR Base and *o*-anisidine-4-sulfondibutylamide. By condensation of (IV) with monoethylaniline and then treatment with 25% ammonia under pressure at 140°, 4-nitroaniline-2-sulfon-*N*-ethylanilide (XI) is obtained.



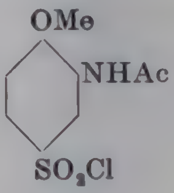
(VII)



(VIII)

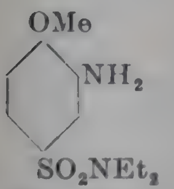


(IX)

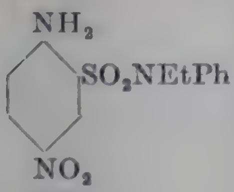


(X)

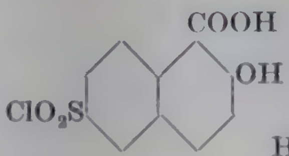
The action of chlorosulfonic acid on 2-hydroxy-1-naphthoic acid at 30–35° yields the 6-sulfonyl chloride (XII). When (XII) is condensed with the neutral sodium salt of K-acid in presence of sodium acetate solution at room temperature, then made alkaline to phenolphthalein and heated at 80°, decarboxylation takes place and acidification gives 2-naphthol-6-sulfonyl-K-acid (XIII).[9] 2-Naphthol-6-sulfonylanthranilic acid (XIV) is prepared similarly.



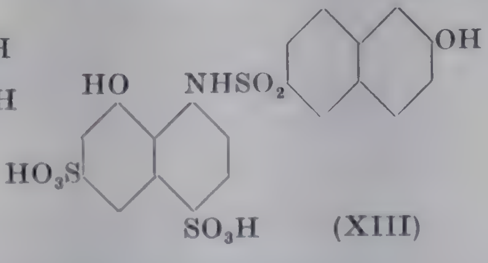
Fast Red ITR Base



(XI)



(XII)



(XIII)

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[129] See p. 83.

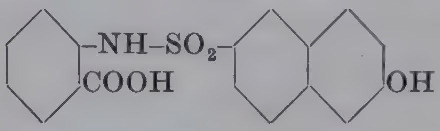
[513] See Chapter XVIII.

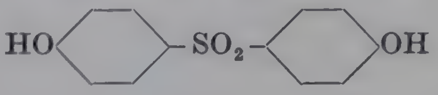
[508] See p. 197.

[9] See p. 50.

The action of 65% oleum at 140–160° on phenol in chlorobenzene-dichlorobenzene solution during 24 hours gives 4,4′-dihydroxydiphenylsulfone (XV) in 95% yield together with a little of the 2,4′-isomer.[235] When

(XIV)



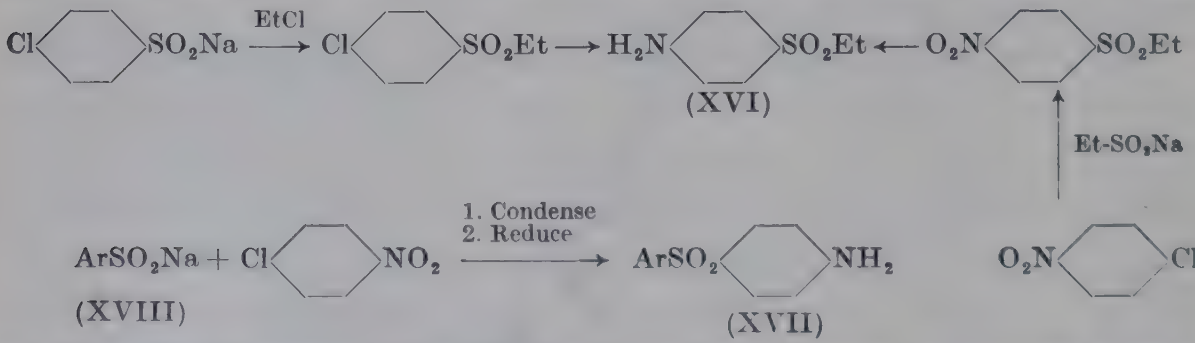


(XV)

(XV) is condensed with paper mill sulfite cellulose liquor and formaldehyde, the resultant resin is a useful tanning agent (Tannigan, IG).[146]

The sulfone group has received considerable attention in dye chemistry during recent years, and many examples of azo dyes and azoic coupling components containing aryl alkyl sulfone groups, introduced with the object of improving level-dyeing character and fastness to light, are mentioned in later chapters.[129, 509] Aryl- and alkylsulfonyl chlorides are intermediates for the preparation of sulfones. Alkylsulfonyl chlorides (e.g., ethylsulfonyl chloride) may be conveniently prepared by the Reed reaction in which an alkane is treated with sulfur dioxide and chlorine ($C_2H_6 + SO_2 + Cl_2 \longrightarrow C_2H_5SO_2Cl + HCl$).[513a] Both aryl- and alkylsulfonyl chlorides can be reduced by means of zinc dust in alcohol or ether to the zinc salt of the corresponding sulfinic acid, isolated as the sodium salt by treatment with aqueous caustic soda. Sulfones are then prepared by condensation of the appropriate sulfinic acid with a reactive chloro compound in presence of sodium acetate or alkali.[514, 515] Aminoaryl sulfones (e.g., XVI) are prepared by heating chloroaryl sulfones with ammonia under pressure[516] or by reduction of nitroaryl compounds.

$$\begin{array}{ll} 2RSO_2Cl + 2Zn \longrightarrow & Zn(RSO_2)_2 + ZnCl_2 \\ & \qquad\downarrow \\ & 2RSO_2Na + Zn(OH)_2 \end{array}$$



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[235] See p. 113.

[146] See p. 89.

[129] See p. 83.

[509] See p. 197.

[513a] Reed, USP 2,046,090; see also Kharasch and Zavist, *JACS* **70,** 3526 (1948). A method for the preparation of aliphatic sulfinic acids is the photochemical reaction of sulfur dioxide with hydrocarbons; Dainton and Ivin, *Trans. Faraday Soc.* **46,** 374 (1950).

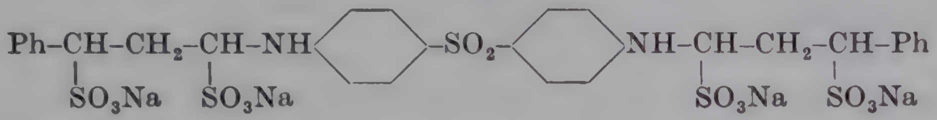
[514] Knoevenagel, *Ber.* **21,** 1349 (1888).

[515] Ullmann and Pasdermadjian, *ibid.* **34,** 1150 (1901).

[516] Ciba, BP 478,624; IG, BP 490,043.

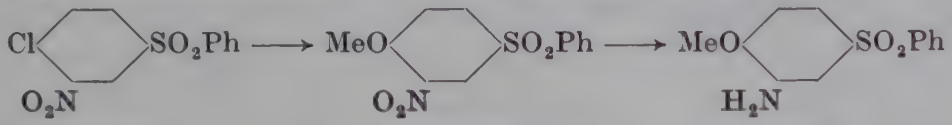
Aminodiaryl sulfones of the type (XVII) have been suggested as Fast Bases, and they can be prepared as indicated. Copper and iodine are useful catalysts and the cellosolves are suitable solvents.[517] The sodium arylsulfinates (XVIII) are obtained by reduction of the arylsulfonyl chloride, e.g., with aqueous sodium sulfite at room temperature[518] or with zinc dust and water[519] at 80–90°, followed by conversion into the sodium salt (XVIII) by means of sodium carbonate.

4,4′-Diaminodiphenylsulfone and its didextrosesulfonate (Promin) are antitubercular agents. Sulfetrone (XIX) has been shown to be effective


(XIX)

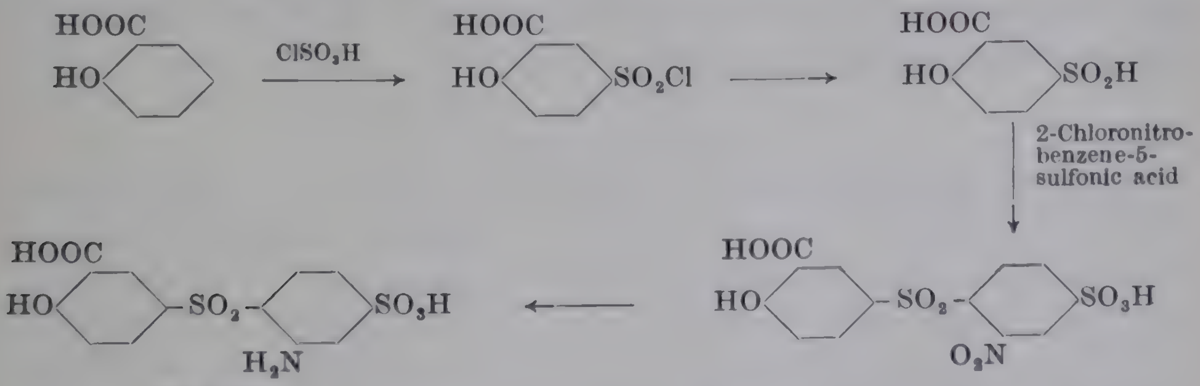
in leprosy.[520]

3-Amino-4-methoxydiphenylsulfone (XX) is obtained by alkoxylation of 4-chloro-3-nitrodiphenylsulfone (XXI) to (XXII) by means of boiling 4%


(XXI) (XXII) (XX)

methanolic caustic soda and reduction of (XXII) with iron and boiling 4% aqueous formic acid.

2-Amino-4′-hydroxy-3′-carboxydiphenylsulfone-4-sulfonic acid (XXIII), produced from salicylic acid by the indicated series of reactions,[10] is an intermediate for pyrazolone dyes.



(XXIII)

Thiophenols. The sulfonyl chlorides are useful intermediates for the preparation of thiophenols, thioglycolic acids, and thioindoxyl derivatives. Thus thiophenol (PhSH, b.p. 169.5°) can be obtained in 91% yield by reduction of benzenesulfonyl chloride in concentrated sulfuric acid with zinc dust.[521] 2,4-Dichlorobenzenesulfonyl chloride (XXIV) gives the corresponding thiophenol (XXV) on reduction with zinc dust and aqueous sulfuric

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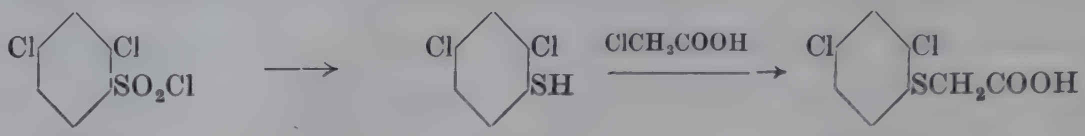
[517] Cf. Kvalnes and du Pont, USP 2,443,255.

[518] Smiles and Bere, *OSCV* I, p. 7.

[519] Whitmore and Hamilton, *ibid.* p. 492.

[520] *Chem. Age* (*London*) **59**, 444 (1948).

[10] See p. 50.

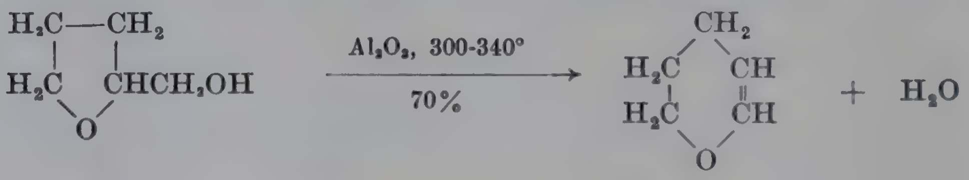


(XXIV) (XXV) (XXVI)

acid at 95°. Condensation of (XXV) in caustic soda solution with chloroacetic acid, first at 0–5° and finally at 95°, followed by acidification, gives 2,4-dichlorophenylthioglycolic acid (XXVI).

FURAN AND PYRAN DERIVATIVES

On account of the large-scale production[522] of furfural from corncobs, oat hulls, and other pentosan-containing agricultural wastes, furan and its derivatives (e.g., furfural, furoic acid) have now become raw materials and intermediates of interest for the organic chemical industries. The dehydration of tetrahydrofurfuryl alcohol (I) gives 2,3-dihydropyran (II) in good yield,[523] so that pyran derivatives also deserve to be considered.[524] Tetrahydrofurfurylamine has been used for condensation with leucoquinizarin to produce cellulose acetate dyes.[525]



(I) (II)

ALIPHATIC COMPOUNDS

Although the consideration of organic intermediates in the wider sense of including aliphatic and heterocyclic compounds used for the organic chemical industries in general (e.g., intermediates for synthetic rubber, synthetic plastics, and detergents) is outside the scope of this book, some aliphatic compounds have present or potential uses in the dyestuff industry as reactants and solvents. The petroleum industry and the synthetic chemical industries based on acetylene have invaded every branch of the organic chemical industry,[525a] and the intermediates for synthetic dyes are no exception. A notable feature of the production of aliphatic compounds is the application of catalytic reactions, particularly in the vapor phase, with resulting development of continuous processes and a steep decline in the cost. It is the object of this section in particular to draw attention to the very valuable reports on such developments in Germany, which have been published since the end of the war.

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[521] Vogt (1861); Adams and Marvel, *OSCV* **I**, p. 504.

[522] Peters, Jr., *Ind. Eng. Chem.* **28**, 755 (1936).

[523] Sawyer and Andrus, *Org. Syntheses* **23**, 25 (1943); see also ICI, BP 547,334.

[524] *Annual Repts. Soc. Chem. Ind. London* **31**, 102 (1946).

[525] Eastman Kodak, USP 2,337,566.

[525a] See Goldstein, The Petroleum Chemicals Industry, Spon, London, 1949.

Among the revealed IG processes for the production of aliphatic chemicals are: ethyl acetate from acetaldehyde and aluminium ethoxide;[526] acetone (95% yield) by treatment of acetic acid in the vapor phase at 400° with cerium oxide;[527] isopropyl alcohol by hydration of propylene;[528] butanol from acetaldehyde via crotonaldehyde;[529, 530] diethylamine (90% yield) by passing acetaldehyde, hydrogen, and ammonia over a nickel (or nickel-chromium) catalyst at 110–150° and recycling mono- and triethylamines;[531, 532] and a series of chlorinated hydrocarbons (methyl chloride, chloroform, trichloroethylene, acetylene tetrachloride, etc.).[533, 529]

The applications of acetylene to the synthesis of organic intermediates have been described in several reports[534, 535] on the IG. The products include butadiene, succinic, glutaric, and adipic acids, maleic anhydride, polyvinylpyrrolidone ("Periston," a blood plasma substitute), vinyl chloride, acrylonitrile, acrylic esters, and ethylene. The advances in the large scale utilization of acetylene[536] for chemical synthesis became possible by the methods developed by the IG for handling acetylene at high pressures and temperatures. These were dependent on dilution with an inert material such as nitrogen and on the design and fabrication of special plant.

Phosgene ($COCl_2$; colorless highly toxic gas liquefying below 8°) is made by the combination of carbon monoxide and chlorine in presence of activated charcoal at 300–400° in a lead-lined steel reactor, and is separated from the starting materials by liquefaction.[146]

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[526] *BIOS* **843.**

[527] *CIOS* Item 22, File XXVI–54.

[528] *FIAT* **968.**

[529] *CIOS* Item 22, File XXV–20.

[530] *BIOS* **713.**

[531] *FIAT* **1081.**

[532] *BIOS* **757.**

[533] *BIOS* **851**; **929**; **1056.**

[534] *BIOS* **350, 354, 358, 359**; *CIOS* Item 22, File XXX–83; and File XXVI–51.

[535] *CIOS* Item 22, File XXII—20.

[536] For a review of the literature on acetylene chemistry, data on the explosive behavior of acetylene and certain mixtures, and the applications of acetylene for vinylation, ethynylation, carboxylation, and cyclic polymerization, see Hanford and Fuller, *Ind. Eng. Chem.* **40,** 1171 (1948); Bergmann, The Chemistry of Acetylene and Related Compounds, Interscience, New York, 1948; Advances in Acetylene Chemistry, Technical Report from Reconstruction Finance Corporation, Office of Rubber Reserve, Research and Development Section, 1945; Copenhaver and Bigelow, Acetylene and Carbon Monoxide Chemistry, Reinhold, New York, 1949; Reppe, Acetylene Chemistry, Meyer and Co., New York, 1949.

[146] See p. 89.

Dimethyl sulfate (b.p. 188°), of which the IG production at Höchst was nearly 3 million pounds, is manufactured by a continuous process,[146] in which dimethyl ether and sulfur trioxide in stoichiometric proportions are introduced into dimethyl sulfate, the temperature being maintained at 40°. Dimethyl sulfate of 99% purity is then obtained by distillation with anhydrous sodium sulfate under reduced pressure.

Formaldehyde (b.p. —21°), used in the dyestuff industry as a methylenating and a condensing agent, is manufactured on a very large scale as an intermediate for Bakelite and for other purposes. The process details for the 100 tons a day plant at IG (Ludwigshafen) have been recently described,[332, 535, 537, 538] dehydrogenation of methanol at 640° in presence of air, steam, and a pure silver catalyst being employed.

Formamide, which is an intermediate for acrylonitrile, from which the Buna N type of synthetic rubber is manufactured, and which has minor uses as a dye intermediate, is obtained by the interaction of methyl formate and ammonia.[539, 540] Methyl formate results from a high pressure synthesis (98–110°/200 atm.) between carbon monoxide and methanol in presence of 1% of sodium ethoxide.[418]

Acetic acid and **anhydride** are used in large quantities in the dyestuff industry for acetylations. Acetic acid is manufactured by the continuous oxidation of acetaldehyde in acetic acid at 50° in presence of a manganese-cerium acetate catalyst (96% yield).[530, 541] Acetaldehyde can be produced from acetylene by hydration in presence of a mercury salt, or by the air oxidation of ethanol in presence of a silver catalyst, or by the dehydrogenation of ethanol vapor over copper at about 280°. In addition to operating the usual mercury-catalyzed hydration of acetylene to acetaldehyde, the IG had developed a process which did not use mercury. Acetylene and methyl alcohol in presence of potassium hydroxide at 160°/16 atm. give methyl vinyl ether, which is hydrolyzed by 0.25% sulfuric acid to acetaldehyde and methyl alcohol, the former being purified by distillation and the latter recycled to the primary operation.[535, 542] A modern process for the manufacture of acetic anhydride is the interaction of ketene and acetic acid ($CH_2{=}CO + CH_3COOH \longrightarrow CH_3CO{-}O{-}COCH_3$). The production of acetic anhydride from acetic acid at IG, Dormagen, has been described.[543] Glacial acetic acid vapor is dehydrated to ketene at 600–720° with triethyl phosphate as catalyst and ketene is absorbed in glacial acetic acid; 90% acetic anhydride is obtained and is then fractionated to 95–97%. Ketene gas can be prepared in the laboratory by the pyrolysis of acetone with use of a "ketene lamp"[544] or other apparatus.[545] Ketene reacts vigorously with phenols, amines, etc., to form acetyl derivatives in excellent yields. Thus acetanilide can be prepared by passing ketene into aniline dissolved in ether.[545] Diketene ($CH_3COCH{=}CO$, b.p. 67–69°/92 mm.) is useful for the synthesis of derivatives of acetoacetic acid such as the acetoacetarylides, which yield yellow dyes and pigments on coupling with diazonium salts.[129] It is prepared[546–548] by dimerization of ketene by allowing the solution in acetone, cooled with dry ice and acetone, to rise to room temperature. A pilot plant operated by IG for the production of ketene and diketene by the Wacker process has been described.[549] Acetic acid, mixed with 0.4% of triethyl phosphate as catalyst, is dehydrated to ketene by passing the vapor at 200–300 mm. pressure through a coil at 730–750° (contact time 0.5–1.0 second); the ketene, stabilized with pyridine or ammonia, is separated from acetic acid and acetic anhydride and dimerized by passing into diketene at −20° in an aluminium absorber.

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[146] See p. 89.

[332] See p. 139.

[535] See p. 203.

[537] *BIOS* **978**.

[538] *BIOS* **1331**.

[539] *FIAT* **925**.

[540] For an account of the properties of formamide, see Magill, *Ind. Eng. Chem.* **26**, 611 (1934).

[418] See p. 161.

[530] See p. 203.

[541] *BIOS* **75**.

[542] *BIOS* **370**.

[543] *FIAT* **145**; see also DRP 403,863.

Ethyl acetoacetate (b.p. 180°) is an important intermediate for dyes, pigments, and pharmaceuticals.[550] When the self-condensation of ethyl acetate in presence of sodium ethoxide is carried out under conditions in which the alcohol formed is removed ($2CH_3COOEt + NaOEt \longrightarrow CH_3COCHNaCOOEt + 2EtOH$), an 80% yield of acetoacetic ester is obtainable.[551] In the IG process at Höchst, a 20% solution of sodium ethoxide is first prepared by dissolving caustic soda in alcohol, adding benzene and removing water by azeotropic distillation. The solution is evaporated down, in a current of nitrogen towards the end, and the anhydrous sodium ethoxide is allowed to react with dry ethyl acetate at the boil. Ethyl acetate is fed in continuously while the alcohol formed is distilled off, the process being continued until the distillate is pure ethyl acetate. The suspension of sodioacetoacetic ester in ethyl acetate is decomposed with sulfuric acid, and acetoacetic ester purified by vacuum distillation. A yield of 85–87% calculated on the caustic soda used is obtained. Ethyl oxalacetate, used for pyrazolone dyes, is prepared as the sodium salt by condensation of ethyl acetate with diethyl oxalate in presence of sodium ethylate at 70° and distilling off alcohol under reduced pressure; benzene can be employed as solvent.

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[544] Williams and Hurd, *J. Org. Chem.* **5**, 122 (1940).

[545] Hurd, *OSCV* I, p. 330.

[129] See p. 83.

[546] Williams and Krynitsky, *Org. Syntheses* **21**, 64 (1941).

[547] Carbide and Carbon Chemicals Corp., BP 410,394.

[548] The preparation of ketenes and ketene dimers has been reviewed by Hanford and Sauer, Organic Reactions III, Wiley, New York, 1946, p. 108–141.

[549] *BIOS* **749.**

[550] For the laboratory preparation of ethyl acetoacetate, which however is commercially available, see Inglis and Roberts, *OSCV* I, p. 235.

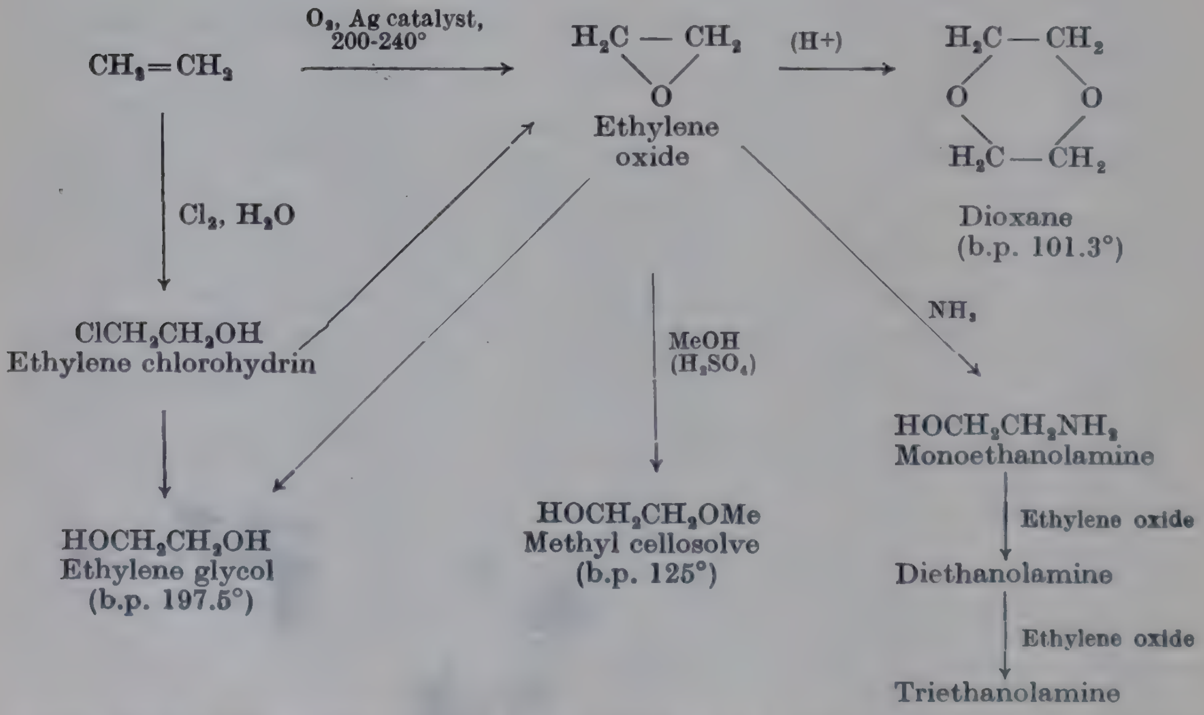
[551] Roberts and McElvain, *JACS* **59**, 2007 (1937).

Ethylene (b.p. −102.4°) is an important basic raw material for the organic chemical industries, and is now manufactured on a large scale by several processes: dehydration of ethanol, cracking of ethane,[552] and hydrogenation of acetylene.[332, 535, 537]

Ethylene oxide (b.p. 13.5°/746.5 mm.) is manufactured[332, 553] by the action of oxygen on ethylene at 200-240° in presence of a silver catalyst; or by conversion of ethylene first into the chlorohydrin by interaction with chlorine and water at 60°, and treatment of the chlorohydrin with slaked lime at 95°. Ethylene bromohydrin (2-bromoethanol), readily prepared[554] from 46% hydrobromic acid and ethylene oxide, is useful in the laboratory as a reagent for the introduction of the β-hydroxyethyl radical. The uses of ethylene oxide products (see Chart 13), such as ethylene glycol as an antifreeze agent, of dioxane and the cellosolves as solvents, and of the ethanolamines as organic alkalis, reagents for synthesis and intermediates for detergents and emulsifying agents are well known. The

CHART 13

ETHYLENE OXIDE PRODUCTS


O_2, Ag catalyst,
200-240°
$CH_2{=}CH_2$
$H_2C — CH_2$
O
Ethylene
oxide
(H+)
$H_2C—CH_2$
O O
$H_2C—CH_2$
Dioxane
(b.p. 101.3°)
Cl_2, H_2O
$ClCH_2CH_2OH$
Ethylene chlorohydrin
MeOH
(H_2SO_4)
NH_3
$HOCH_2CH_2NH_2$
Monoethanolamine
Ethylene oxide
Diethanolamine
Ethylene oxide
Triethanolamine
$HOCH_2CH_2OH$
Ethylene glycol
(b.p. 197.5°)
$HOCH_2CH_2OMe$
Methyl cellosolve
(b.p. 125°)

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[552] *BIOS* 877.

[332] See p. 139.

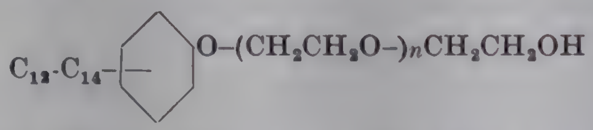
[535] See p. 203.

[537] See p. 204.

[553] McBee, Haas, and Wiseman, *Ind. Eng. Chem.* **37**, 432 (1945); *BIOS* **686**; **360.**

[554] Thayer, Marvel and Hiers, *OSCV* I, p. 117.

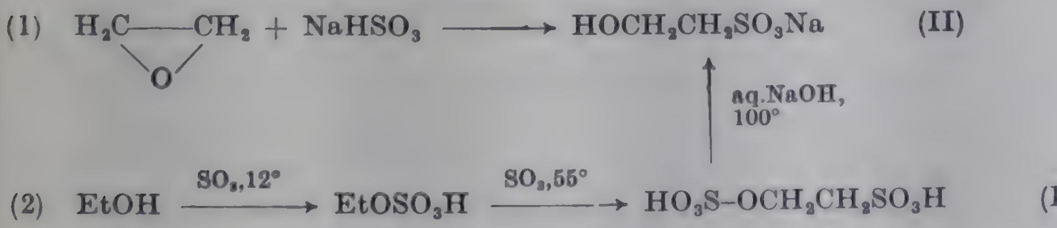
action of sodium sulfide on ethylene chlorohydrin gives β-thiodiglycol ($HOCH_2CH_2SCH_2CH_2OH$, b.p. 164–166°/20 mm.),[555] a useful solvent employed in calico printing of vat colors. Gaseous ethylene oxide and hydrogen sulfide react in thiodiglycol at 45–60° to give thiodiglycol in quantitative yield.[556] The corresponding dichloride, for the production of which the treatment of the nontoxic thiodiglycol with hydrochloric acid may be utilized, is the well-known poison gas "mustard gas." β-Phenylethyl alcohol, a valuable perfume occurring naturally in rose oil, can be prepared[235, 557] in 55–60% yield by condensation of benzene with ethylene oxide in presence of aluminium chloride at 5°; β-phenylethyl chloride and dibenzyl are by-products. β-Phenylethyl alcohol can also be prepared by the action of ethylene oxide on phenylmagnesium chloride. The action of one mole of ethylene oxide on phenol yields glycol monophenyl ether ($PhOCH_2CH_2OH$), which is a bacteriostatic and bactericidal agent ("Phenoxetol"). By the condensation of *C*-alkylphenols with ethylene oxide, IG prepared a series of wetting agents and detergents ("Igepals"), which had the advantage that no fats were required for their production. They have the general structure (I), in which there is one long *C*-alkyl chain of 12 to 14



(I)

carbon atoms or two shorter ones of 6 to 7, and *n* is 5 to 8 or 8 to 11 according as the detergent is used on wool or on cotton. The hydroxyl group can be sulfated, and the commercial products are usually mixtures of (I) with the more soluble sodium salts of the sulfuric esters.[558]

Sodium β-hydroxyethylsulfonate (II) is an intermediate for wetting agents, such as Igepon A (IG). Two methods of preparation[6] are available: (1) the interaction of ethylene oxide and sodium bisulfite, and (2) the



action of 100% oleum on ethanol successively to form ethyl hydrogen sulfate and the hydrogen sulfate (III) of β-hydroxyethylsulfonic acid, (III) being then hydrolyzed to (II). On reaction of (II) with 25% aqueous methylamine in presence of a little caustic soda at 280° and 200 atmospheres pressure, a continuous process being suitable, the sodium salt (IV) of *N*-methyltaurine is produced. By use of ammonia in place of methylamine taurine is similarly prepared.[559] The *N*-oleyl derivative of (IV) is the well-known wetting agent, Igepon T (IG), and (IV) is also used in making intermediates for cellulose acetate dyes. An example of such an intermediate is 4-nitro-2-sulfophenylmethyltaurine (V), prepared by heating (IV) with

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[555] Meyer (1886); Faber and Miller, *ibid.* II, p. 576.

[556] Woodward, *JCS* 1892 (**1948**).

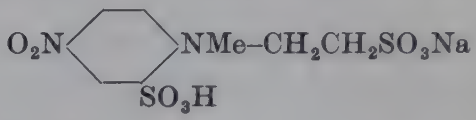
[235] See p. 113.

[557] Calco, USP 2,125,490; Dow Chemical Co., BP 487,038; IG, BP 457,022.

[558] *BIOS* **418.**

[6] See p. 50.

(IV) $MeNH{-}CH_2CH_2SO_3Na$


(V)

4-chloronitrobenzene-3-sulfonic acid in aqueous solution at the boil in presence of calcined magnesia.[6] Reduction gives the corresponding amine from which azo dyes for cellulose acetate can be obtained.

Alkylamines, notably mono-, di-, and trimethylamines,[560] are made directly from ammonia and the alcohol in presence of dehydrating catalysts.[561] An important route to alkylamines is the catalytic hydrogenation of nitriles in presence of Raney nickel, the nitriles being obtained by passing the mixed vapors of the aliphatic acid and ammonia over an alumina catalyst at about 400°. The excess ammonia is recycled, and a 99% conversion can be obtained under optimum conditions. A method for the production of higher fatty amines is the hydrogenation of amides or of ammonium salts in the liquid phase promoted with a copper chromite catalyst.[562] A convenient laboratory preparation of methylamine hydrochloride involves reaction of formalin with ammonium chloride at 104° for a few hours;[563] and trimethylamine hydrochloride (and from it trimethylamine) can be prepared by heating[564] paraformaldehyde with ammonium chloride at 85–160°.

$$3(CH_2O)_3 + 2NH_4Cl \longrightarrow 2(CH_3)_3NHCl + 3CO_2 + 3H_2O$$

Glycerine is used in the dyestuff industry in the preparation of the important intermediate benzanthrone. Like ethylene chlorohydrin and ethylene oxide, epichlorohydrin (VI; b.p. 115–117°) is useful for the preparation of intermediates for cellulose acetate dyes ; (VI) is obtained in

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[559] For the laboratory preparation of taurine from ethylene dibromide, see Marvel, Sparberg, and Bailey, *OSCV* II, pp. 558, 563.

[6] See p. 50.

[560] For methods of separation of the methylamines, see IG, BP 421,486; 422,139; 422,563–4; 425,486; 435,404; du Pont, BP 436,874.

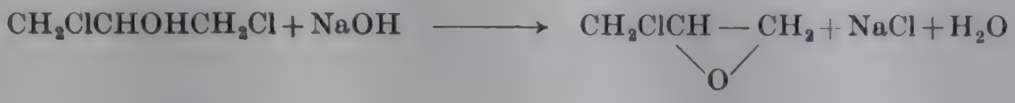
[561] du Pont, BP 384,714; 410,500; IG, BP 406,700; Röhm and Haas Co., BP 399,201; 394,475.

[562] Adkins and Wojcik, *JACS* **56**, 247 (1934).

[563] Marvel and Jenkins, *OSCV* I, p. 347.

[564] Adams, Brown, and Marvel, *ibid.* 531, 528.

80% yield by the treatment of glycerol α,γ-dichlorohydrin (VII)[565] in ether with caustic soda.[566]



$$CH_2ClCHOHCH_2Cl + NaOH \longrightarrow CH_2ClCH{-}CH_2 (\text{-O-}) + NaCl + H_2O$$

(VII) (VI)

Chloroacetic acid (m.p. 63°; b.p. 189.5°) is made [235, 566–568] by the hydrolysis of trichloroethylene with 75% sulfuric acid at 130–140° ($CHCl{=}CCl_2 + 2H_2O \longrightarrow ClCH_2COOH + 2HCl$), or by the older method of chlorinating acetic acid in presence of 3% of acetic anhydride and 0.7% sulfur.[569]

Sarcosine, used for stabilizing diazonium salts,[41] is obtained[6] as an 18–19% solution of the sodium salt by agitating sodium chloroacetate solution with a large excess of aqueous methylamine (15 moles) at 15° for 24 hours, making alkaline, distilling off excess methylamine, and concentrating ($MeNH_2 + ClCH_2COONa \longrightarrow MeNHCH_2COONa$).

By the addition of a primary or secondary aromatic amine to acrylic, methacrylic, crotonic, or similar unsaturated acid, an amino acid is formed; thus aniline and acrylic acid give β-anilinocrotonic acid. In place of the unsaturated acid, its ester, amide or nitrile may be used, and it is probable that some of these amino acids and their derivatives will be of interest as dye intermediates.[570] The reaction incidentally provides a method of introducing solubilizing groups into intermediates and dyes.

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[565] Conant and Quayle, *ibid.* p. 292.
[566] Clarke and Hartman, *ibid.* p. 233.
[235] See p. 113.
[567] *CIOS* Item 22, File XXVI–11.
[568] *FIAT* **1059.**
[569] *BIOS* **929.**
[41] See p. 57.
[6] See p. 50.
[570] IG, BP 478,304.

Chapter IV

DIAZOTIZATION AND DIAZONIUM SALTS

Discovered by Peter Griess in 1860, the most important reaction of the aromatic primary amines is the formation of diazonium salts on treatment with nitrous acid. The diazonium salts are indispensable intermediates for the preparation of azo dyes and are also useful, both in the laboratory and in technical practice, for the replacement of an amino group by hydroxyl, halogen, cyanogen, and other groups.

Diazotization Methods

Diazotization[1-3] proceeds according to equation (1). Sodium nitrite is employed in theoretical quantity, but the acid must be in excess in order to prevent partial diazotization and condensation of the diazonium salt

$$ArNH_2 + NaNO_2 + 2HCl \longrightarrow ArN_2Cl + NaCl + 2H_2O \qquad (1)$$

with the undiazotized amine to form the diazoamino compound(I);[4] excess mineral acid also stabilizes the diazonium salt by inhibition of decomposition due to other secondary reactions. The molar proportion of acid

$$ArN_2Cl + H_2N\text{–}Ar \longrightarrow Ar\text{–}N{=}N\text{–}NH\text{–}Ar \qquad (I)$$

usually necessary is 2.5–3, but for many amines, such as *p*-nitroaniline, as much as 6–7 moles can be used with advantage. If diazotization is to proceed satisfactorily the amine must be in solution in the aqueous acid or the amine hydrochloride must be in a very fine state of suspension. Aminoazotoluene hydrochloride is obtained in an easily diazotizable form by heating the base with 3–5% hydrochloric acid at 90–100° for a few minutes.[5] The addition of sodium nitrite is carried out at 0–5° on account of the instability of diazonium salts; higher temperatures up to or even more than 20° are permissible for some diazonium salts. Completion of diazotization and a slight excess of nitrous acid are tested for by starch-iodide. 4,4′-Diaminodiphenylmethane–2,2′-sulfone gives a blue color with nitrous acid, and is stated to provide a better test for excess nitrous

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[1-3] For a complete account of the preparation, properties and constitution of diazo compounds, see (1) Hantzsch and Reddelien, Die Diazoverbindungen, Springer, Berlin, 1921; (2) Saunders, The Aromatic Diazo-Compounds and their Technical Applications, Arnold, London, 1949; (3) Holzach, Die Aromatischen Diazoverbindungen, Enke, Stuttgart, 1947.

[4] Hartman and Dickey, *OSCV* II, p. 163.

[5] Richardson and du Pont, USP 2,346,508.

acid than starch-iodide.[6] The diazonium salt solution is then used for the coupling or other reaction as soon as possible. Clarity of the solution, which is often filtered immediately before use in an azo dye preparation, and absence of foam are indications of successful diazotization without decomposition. Technical diazotizations are carried out in wooden vats or rubber-lined kettles, since metals catalyze the decomposition of diazonium salts; in handling diazonium salt solutions their tendency to decompose by the action of heat and light has also to be remembered.

The slight excess of nitrous acid at the end of a diazotization process is normally immaterial in a technical coupling reaction, but in the laboratory and where there is danger of nitrous acid reacting with the second component, it can be destroyed by means of urea. Sulfamic acid can also be employed; in leather dyeing and in the preparation of azo pigments brighter shades are thus obtained.[7] However, several diazonium salts react with sulfamic acid[8] even in strongly acid solution according to the net equation: $RN_2OH + NH_2SO_3H \longrightarrow RNH_2 + H_2SO_4 + N_2$

Facile diazotization depends on the basicity of the amine. Negatively substituted and therefore weakly basic amines (e.g., 2,4-dinitroaniline, 2,6-dibromo-4-nitroaniline) are diazotized only by special methods. Difficulties in diazotization can also arise because of the large molecular weight of the amine, sparing solubility in aqueous acid, or oxidizability. Among the numerous processes which have been suggested for amines not amenable to simple diazotization in aqueous acid solution with sodium nitrite, a few are mentioned.

(1) The amine (e.g., 2,4-dinitroaniline) is added to a solution of sodium nitrite in concentrated sulfuric acid. Schoutissen[9] has shown that a modification of this method is successful for *p*-aminobenzaldehyde, *p*-phenylenediamine, and trichloro-*p*-phenylenediamine; the amine is dissolved in concentrated sulfuric acid, cooled to 0°, treated with nitrosylsulfuric acid (sodium nitrite in concentrated sulfuric acid), and then run into phosphoric acid (d. 1.70) at 0°. After 30 minutes urea is added, and the reaction mixture poured on ice when a clear solution of the diazonium salt is obtained.

(2) The very finely powdered base (e.g., α-aminoanthraquinone)[10] is made into a paste with concentrated hydrochloric acid, by boiling and then cooling to 10° if necessary, solid sodium nitrite is added, and after 20 minutes the mixture is stirred into water at 10°.

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[6] *BIOS* 961.

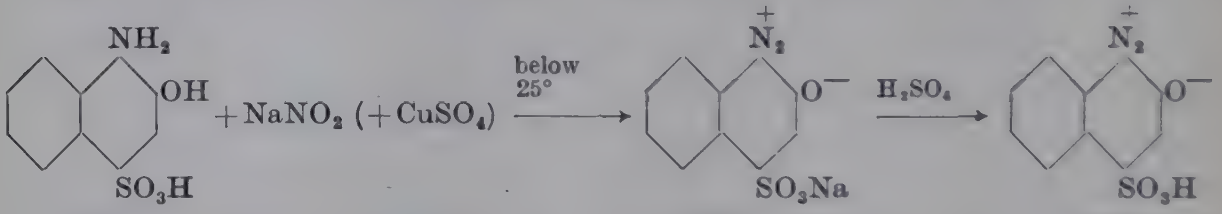
[7] Lubs and du Pont, USP 2,160,882.

[8] Grimmel and Morgan, *JACS* **70**, 1750 (1948).

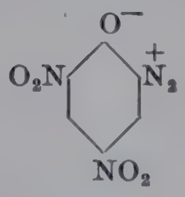
[9] Schoutissen, *ibid.* **55**, 4531, 4535 (1933).

[10] Moualim and Venkataraman, IP 33,261.

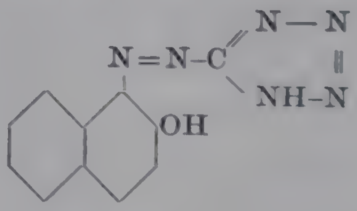
(3) *o*-Aminophenols and *o*-aminonaphthols, which are intermediates for mordant dyes, present difficulties in diazotization owing to their tendency to undergo oxidation. A suitable procedure is to effect diazotization in presence of a copper salt, and is exemplified by the diazotization of 1-amino-2-naphthol-4-sulfonic acid (II), an important intermediate for metallizable dyes. When (II) in the form of an aqueous paste is added to a solution of sodium nitrite containing copper sulfate (about 0.3% of the weight of II), (III) is formed; after the mixture is rendered just acid by the addition of sulfuric acid, the solution is clarified; when excess sulfuric acid is added to the filtrate, (IV) separates as a sandy greyish-orange product, which can be collected, dried at about 50°, and stored.[10a] Picramic acid also forms a diazo oxide, or " diazodinitrophenol anhydride " (V), on treatment with nitrous acid. Diazodinitrophenol, an explosive primer,[11] can be prepared in the form of free-flowing crystals by diazotization of a salt of picramic acid in presence of aromatic amines or phenols, e.g., the mother liquors from the precipitation of diazodinitrophenol and its products of decomposition by alkali.[12]



(II) (III) (IV)



(V)



(VI)

(4) Picramide (2,4,6-trinitroaniline) can be diazotized without decomposition by solution in glacial acetic acid and addition of nitrosylsulfuric acid.[13] In the case of amines in which nuclear nitrosation occurs during diazotization in sulfuric acid solution, smooth diazotization can be effected and the diazonium sulfate separated in crystalline form by diazotization in sulfuric acid-glacial acetic acid solution and addition of ether;[14] the diazonium sulfate is filtered off and freed from acid by washing with ether

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[10a] *BIOS* **1363.**

[11] Dehn, USP 1,404,687.

[12] Alexander, USP 2,103,926.

[13] Misslin, *Helv. Chim. Acta* **3,** 626 (1920).

[14] Hodgson and Walker, *JCS* 1205, 1620 (**1933**); Hodgson and Turner, *ibid.* 86 (**1943**).

or ethyl acetate. The yields are of the order of 70–100%, and all diazotizable amines, including the nitro- and bromonaphthylamines, are amenable to this treatment.[15] A typical procedure consists in stirring a cold solution of the amine (1 g.) in glacial acetic acid (10 cc.) into the required amount of sodium nitrite (usually about 1 g.) dissolved in sulfuric acid (5 cc., d. 1.84) at 0°. The mixture is kept for 10–30 minutes, when diazotization is complete. Ether (50 cc. or more) is stirred into the mixture, when the solid diazonium sulfate separates and is filtered; the mixed acid is removed by washing with ether-glacial acetic acid, and finally with ether.

A solution of the amine in pyridine or quinoline can be added to nitrosylsulfuric acid.[16]

(5) Knoevenagel's method[17] for preparing diazonium salts in the solid state by suspension of the dry amine salt in alcohol (or glacial acetic acid)[18] and treatment with an alkyl nitrite is still valuable as a laboratory method, if other procedures are not suitable. The diazonium salt is precipitated by addition of ether. If the salt tends to separate in a sticky form owing to the water formed in the reaction, solvents immiscible with water, such as carbon tetrachloride or benzene, can be used together with a dehydrating agent such as sodium sulfate.[19]

Diazonium salts can be prepared by methods other than the diazotization of a primary amine, e.g., by the oxidation of an arylhydrazine with a halogen. Although these methods have no technical value, they have interest from the point of view of the constitution of diazonium salts and in special cases are useful in the laboratory. As a development of Bamberger's observation[20] that nitrosobenzene is converted into phenyldiazonium nitrate by nitric oxide ($\mathrm{Ph{-}NO + 2NO \longrightarrow Ph\overset{+}{N_2}\overset{-}{NO_3}}$), it has been recently shown that diazonium nitrates can be prepared in good yield by the action of nitric acid and sodium nitrite on phenylmercuric nitrate.[21]

An aliphatic amine which undergoes "diazotization" smoothly under the right conditions of agitation and pH control is aminoguanidine;[22] the diazo compound, like an aryldiazonium salt, couples with phenols and amines. The dyes obtained by coupling with naphthylamines and naphthols dye wool fast shades of yellow, orange, and reddish-brown,[23] but the reaction is more complicated than the coupling of an aryldiazonium salt. With β-naphthol, for instance, the product of the action of " diazotized " aminoguanidine is 1,2,3,4-tetrazole-5-azo-β-naphthol (VI).[24]

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[15] Hodgson and Mahadevan, *ibid.* 325 (**1947**).

[16] de Milt and Van Zandt, *JACS* **58,** 2044 (1936).

[17] *Ber.* **23,** 2995 (1890).

[18] Hantzsch and Jochem, *ibid.* **34,** 3337 (1901); see also Schoutissen, *Rec. trav. chim.* **40,** 763 (1921).

[19] Ciba, DRP 575,832.

[20] Bamberger, *Ber.* **30,** 512 (1897).

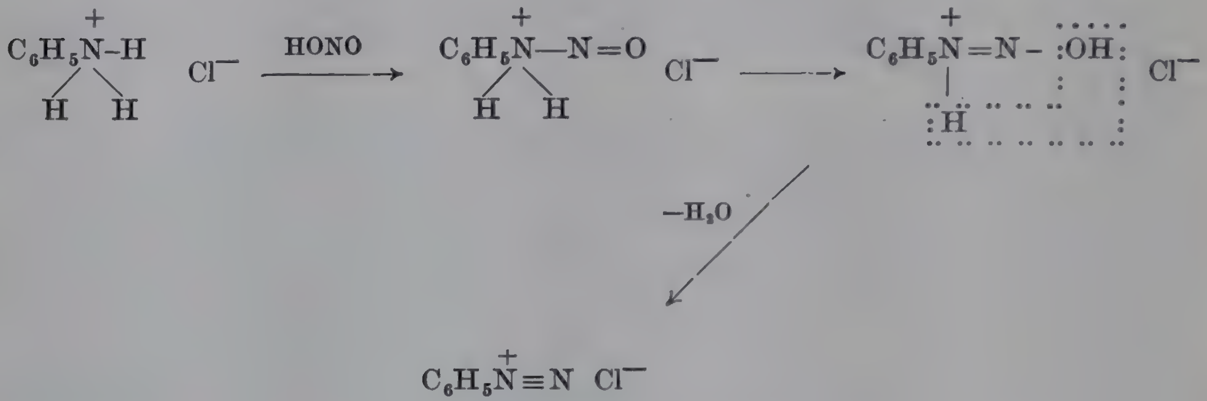
[21] Westheimer, Segel, and Schramm, *JACS* **69,** 773 (1947); and other references quoted in the paper.

[22] Curtius, *Ann.* **314,** 339 (1900).

[23] Shreve, Carter, and Willis, *Ind. Eng. Chem.* **36,** 426 (1944).

THE MECHANISM OF DIAZOTIZATION

Conclusive evidence regarding the actual stages involved in the transformation of a primary amine into a diazonium salt has not yet been adduced. A suggested intermediate[25] is the *N*-nitroso derivative. According to this mechanism diazotization of aromatic amines involves interaction of the arylammonium ion $ArNH_3^+$, formed by ionization of the amine salt, with undissociated nitrous acid. Experimental facts partly accord with this view. The amount of acid present must be sufficient to prevent hydrolysis of the amine salt; the rate of diazotization is nearly independent of the excess of acid that is in fact normally present during a diazotization.



Benzenediazonium chloride

Schmid and Muhr[26] have investigated the kinetics of the action of nitrous acid on aniline. The rate law in aqueous sulfuric acid is:

$$v = \frac{k_1(C_6H_5NH_3^+)\ (HNO_2)^2}{K_b(OH_3^+)} = k_1(C_6H_5NH_2)\ (HNO_2)^2$$

and that in hydrochloric acid:

$$v = (C_6H_5NH_2)\left[k_1\ (HNO_2)^2 + k_2\ (HNO_2)\ (OH_3^+)\ (Cl^-)\right]$$

Hammett[27] suggests that the rate-determining steps involve aniline base and either nitrogen trioxide (N_2O_3) or nitrosyl chloride (NOCl). Since nitrous acid derivatives, at least in one of the resonance structures, contain a nitrogen atom with only six electrons, attachment of the nitrogen atom to the unshared pair of electrons on the amine nitrogen takes place and a N–N linkage is formed. The final product is the diazonium ion.

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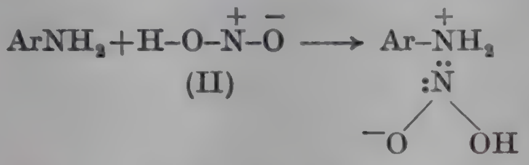
[24] Reilly, Teegan, and Carey, *Nature* **159**, 643 (1947).

[25] Fieser and Fieser, Organic Chemistry, p. 618, D. C. Heath, Boston, 1944. See also Earl and Hills, *Chemistry and Industry* **60**, 889 (1941); Hodgson, *J. Soc. Dyers Colourists* **65**, 226 (1949); Grachev, *J. Gen. Chem. U.S.S.R.* **18**, 848 (1948).

[26] Schmid and Muhr, *Ber.* **70B**, 421 (1937).

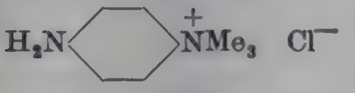
[27] Hammett, Physical Organic Chemistry, McGraw-Hill, New York, 1940, p. 294.

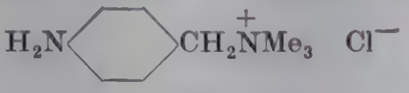
A feasible mechanism involves formation of the complex (I) by attachment of the nitrogen of the base to the nitrogen atom with a sextet of electrons in the resonance structure (II) of nitrous acid; the complex

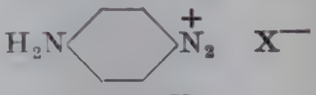

(II) (I)

then reacts with a proton with loss of water and formation of the diazonium cation.

Amines of different basicities diazotize at rates which follow the order of the basicities; the less basic an amine, the less is the tendency for the nitrogen atom to attract a proton and become an ammonium ion, and the slower is the diazotization under conditions of limited acidity. The amine (III) has a lower velocity constant than the amine (IV), when the diazotizations are carried out in the absence of excess acid;[28] in (III) the basic


(III)


(IV)


(V)

character of the amino group is reduced by the positive charge on the nitrogen atom in the *p*-position, whereas in (IV) the methylene group insulates the aromatic ring from the influence of the positive charge, so that the amino group is much more basic than in (III) and diazotizes faster. When hydrochloric acid is present in excess, both (III) and (IV) diazotize at practically the same rate.

One amino group in *p*-phenylenediamine diazotizes much more easily than the second; the positive charge on the diazonium group in the *p*-aminophenyldiazonium salt (V) tends to inhibit diazotization.[9] *p*-Aminodimethylaniline, in which in acid solution the positive charge on the $NHMe_2$ group is weaker, diazotizes quantitatively, although slowly.[29]

A method for estimating the "speed of diazotization" has been suggested,[30] in which advantage is taken of the slow diazotization of benzidine. A mixture of 0.5 mole of benzidine and one mole of an aromatic primary amine is treated with hydrochloric acid and one mole of sodium nitrite, and the amount of undiazotized benzidine is estimated as the insoluble sulfate.

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[28] Reilly and Drumm, *JCS* 871 (1935).

[29] Ayling, Gorvin and Hindel, *JCS* 613 (1941).

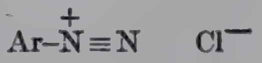
[30] Rostovtzeva, *Z. anal. Chem.* **105,** 32 (1936).

[9] See p. 211.

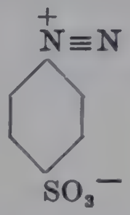
CONSTITUTION AND REACTIONS OF DIAZONIUM SALTS

The solubility of the diazonium salts in water, the insolubility in ether and other organic solvents, the electrical conductivity of the aqueous solutions, and other reactions closely analogous to those of ammonium salts are consistent with the constitution (I). They are dissociated in aqueous solution to organic cations and chloride anions. When sulfanilic acid is diazotized, the sparingly soluble inner or dipolar salt (II) crystallizes from the solution. Like ammonium and alkali salts, diazonium salts form double compounds with zinc, copper, gold, and platinum chlorides; the ability to form such double salts is utilized in the production of diazonium salts in solid, stable form.

(I)

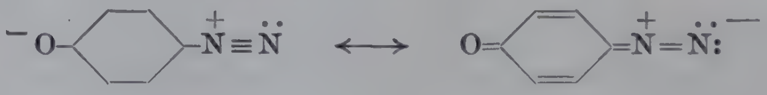


$Ar{-}\overset{+}{N}{\equiv}N \quad Cl^{-}$



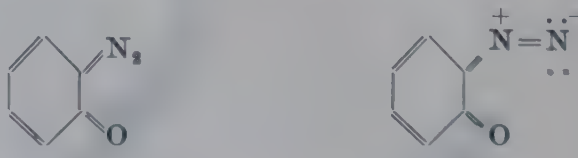
(II)

The diazo oxides (also called diazophenols) formed by the action of nitrous acid on *o*- and *p*-aminophenols (or by other methods[31]) are colored. The properties of the diazo oxides including their color, sparing solubility in water, solubility in nonpolar solvents, stability and slow coupling, are best explained by formulation as resonance hybrids of the structures (IIIA) and (IIIB). From dipole moment measurements it appears probable[32] that the diazo oxides from *o*-aminophenols have the structure (IVA) or (IVB).



(A) (B) (III)

This is further supported by the inability of *m*-aminophenols to form such diazo oxides and the similarity of the absorption spectra of the diazo oxides and of the aliphatic diazo compounds. In ether solution diazophenols and diazo-naphthols produce absorption spectra which are similar to those of the corresponding quinones.[33]



(A) (B) (IV)

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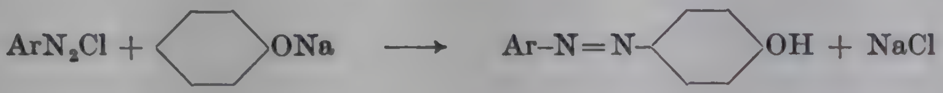
[31] Hodgson and Birtwell, *JCS* 321 (**1943**); Hodgson and Marsden, *J. Soc. Dyers Colourists* **59**, 271 (1943).

[32] Anderson and Le Févre, *Nature* **162**, 450 (1948). See also *JCS* 2082 (**1949**).

[33] Anderson and Roedel, *JACS* **67**, 955 (1945).

Diazonium salts undergo two types of reactions: (*a*) those in which nitrogen is retained, as in diazo coupling and in reduction to arylhydrazines; and (*b*) those in which nitrogen is evolved, such as the Sandmeyer reaction, hydrolysis to phenols, reduction to hydrocarbons, condensation to form diaryls, and Bart's and other reactions for the preparation of organic arsenicals, antimonials, etc.

The most important property of diazonium salts is their ability to react ("couple") with phenols, amines, and certain other components with formation of azo dyes by attachment of the aryldiazo group to a carbon atom. The reaction is discussed in detail in Chapter XI.



Snow[34] has measured the rate of decomposition of various diazonium chlorides at 20°, and has arranged them in the following order of decreasing stability: *p*-chloroaniline, *m*-nitroaniline, *m*-6-nitro-4-xylidine, *o*-nitroaniline, *o*-anisidine, *p*-nitroaniline, *p*-bromoaniline, *o*-phenetidine, *p*-iodoaniline, 5-aminosalicylic acid, *p*-toluidine, aminoazobenzene, *p*-aminophenol, *p*-phenylenediamine (diazotized), picramic acid, sulfanilic acid, *p*-aminobenzoic acid, α-naphthylamine, *p*-anisidine, β-naphthylamine, *m*-4-xylidine, anthranilic acid, aminoazotoluene, *m*-aminobenzoic acid, *o*-4-xylidine, *o*-3-xylidine, aniline, *o*-toluidine, *m*-toluidine, *m*-anisidine, *p*-xylidine, *p*-phenylenediamine (tetrazotized). Electronegative substitution of the amine increases the stability of the diazonium salt. Increased concentration often increases the stability of a diazonium salt. Diazonium sulfates are more stable and the acetates less stable than the chlorides.

The decomposition of phenyldiazonium chloride in dilute hydrochloric acid is a first-order reaction; the heat of activation is 27,200 cal./g. mol. The nature of the decomposition products and the reaction velocity are functions of the concentration of the diazonium solution. The stability of phenyldiazonium chloride is decreased by *m*-hydroxy, *o*- or *m*-methyl, *m*-methoxy, and *o*- or *m*-phenyl substitution. Substitution by chlorine, carboxyl, sulfonic or nitro groups, and by methyl, hydroxyl, methoxyl, or phenyl in positions other than those mentioned earlier increases the stability of the diazonium salt.[35]

The decomposition of *o*-methoxybenzenediazonium chloride in aqueous acid solution is characterized by an induction period.[36] As in the case of the 5-nitro derivative,[37] the diazo oxide is formed as an intermediate product. Infrared spectral evidence of the presence of methyl chloride in the evolved nitrogen has been obtained.[38] It has also been observed that demethylation of an *o*- or *p*-methoxy group takes place in acid solution during diazotization of an amine, if there is a nitro group *ortho* to the methoxyl.[39] *o*-Hydroxyphenyldiazonium salts undergo a remarkable photodecomposition to cyclopentadienecarboxylic acid.[39a]

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[34] Snow, *Ind. Eng. Chem.* **24,** 1420 (1932).

[35] Crossley, Kienle, and Benbrook, *JACS* **62,** 1400 (1940).

[36] Crossley *et al., ibid.* **69,** 1160 (1947).

[37] Noelting and Steimle, *Bull. soc. chim. France* **17,** 392 (1915).

The Sandmeyer and similar reactions by which a primary amino group is replaced by hydrogen,[40] halogen,[41] nitrile,[42] nitro,[43] and other groups, via the diazonium salt, constitute very useful synthetical methods. Diazonium salts stabilized as the fluoborates are useful for the preparation of fluoro compounds. Fluorobenzene can be prepared in this manner from aniline by careful thermal decomposition of phenyldiazonium fluoborate;[44] and *p*-fluorobenzoic acid is available from ethyl *p*-aminobenzoate.[45] The preparation of *p*-dinitrobenzene by the Sandmeyer reaction on *p*-nitrophenyldiazonium fluoborate has been described.[46] Thiophenols can be prepared by the treatment of aryldiazonium chlorides with potassium ethyl xanthogenate and then heating with alkali, but the reaction is explosive under certain conditions.[47] Symmetrical diaryls such as diphenic acid can be prepared by treatment of diazonium salts with cuprous salts.[48] Asymmetrical diaryls can be prepared by the interaction of diazo compounds with liquid aromatic compounds.[49] α- and γ-Arylpyridines can be synthesized by the decomposition of aryldiazonium salts in presence of pyridine.[50] Interaction of furan with diazonium salts in presence of alkali leads to 2-arylfurans, with minor quantities of the 3-isomer.[51]

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[38] Woodward and Ebert, Jr., *JACS* **70,** 1666 (1948).

[39] Meldola and Hay, *JCS* **91,** 1474 (1907).

[39a] de Jonge *et al., Rec. trav. chim.* **68,** 430 (1949).

[40] Kornblum in Organic Reactions, II, Wiley, New York, 1944, p. 262; Alexander and Burge, *JACS* **70,** 876 (1948).

[41] For the preparation of *o*- and *p*-chlorotoluene and *o*- and *p*-bromotoluene see Marvel and McElvain, *OSCV* I, p. 170; Bigelow, *ibid.* p. 135; for the preparation of *m*-chloronitrobenzene see Hartman and Brethen, *ibid.* p. 162.

[42] For the preparation of *o*- and *p*-tolunitrile see Clarke and Read, *ibid.* p. 514.

[43] For the preparation of 1,4-dinitronaphthalene, see Hodgson, Mahadevan, and Ward, *Org. Syntheses* **28,** 52 (1948).

[44] Balz and Schiemann, *Ber.* **60,** 1188 (1927); du Pont, USP 1,916,327; Flood, *OSCV* II, p. 295.

[45] Schiemann and Winkelmüller, *ibid.* p. 299.

[46] Starkey, *ibid.* p. 225.

[47] Bourgeois (1895); see also Nawiasky, Ebersole, and Werner, *Chem. Eng. News* **23,** 1247 (1945).

[48] Atkinson and Lawler, *OSCV* I, p. 222; Atkinson, Lawler, *et al., JACS* **63,** 730 (1941).

[49] Bachmann and Hofmann in Organic Reactions, II, Wiley, New York, 1944, p. 224.

[50] Heilbron *et al., JCS* 349 (**1940**); *et sequa.*

[51] Johnson, *ibid.,* 895 (**1946**).

In the Pschorr reaction (1896) for the synthesis of phenanthrene-9-carboxylic acid, diazotized α-phenyl-*o*-aminocinnamic acid is treated with copper powder; and similar syntheses of polycyclic compounds (e.g. fluorene, fluorenone, 4,5,9,10-dibenzopyrene) by the elimination of nitrogen from a diazonium salt and intramolecular cyclization have been described.[51a] Another recent application of a diazonium salt decomposition for a synthetical purpose is the Meerwein reaction. Diazonium salts, in presence of sodium acetate and acetone or pyridine, add to α,β-unsaturated compounds such as the esters of cinnamic and fumaric acids; and by modification of the experimental procedure stilbenes can be synthesized from cinnamic acids.[52]

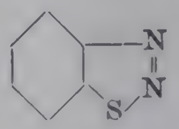
$$\text{Ph–CH=CH–COOH} + \text{PhN}_2\text{Cl} \longrightarrow \text{Ph–CH=CH–Ph} + \text{CO}_2 + \text{N}_2 + \text{HCl}$$

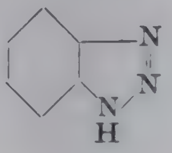
Aryldiazonium chlorides containing negative substituents react with citraconic and mesaconic acids in presence of acetone, sodium acetate, and copper chloride to form α-methyl-β-arylacrylic acids, and not the ββ-isomer; the result supports Koelsch's free radical mechanism for such condensations.[53]

Abnormal products of diazotizations arise from such reactions and decompositions, which often have preparative value. Thus the action of nitrous acid on 4-aminoquinoline readily yields 4-hydroxyquinoline, whereas 3-aminopyridine and 3-aminoquinoline undergo normal diazotization. *o*-Aminoarylmercaptans yield diazo sulfides, or thiadiazoles (V), which differ from the diazo oxides in being colorless and much more stable.[54]

o-Phenylenediamine gives 1,2,3-benzotriazole (VI) in 80% yield on treatment with nitrous acid.[55] The action of nitrous acid on *o*-toluidines in acetic acid results in cyclization of the intermediate diazo hydroxides to indazoles;[56] thus 5-nitro-*o*-toluidine gives 5-nitroindazole (VII) in about 80% yield.[57] An interesting instance of the influence of the diazonium

(V)





(VI)

[51a] E.g., see DeTar and Sagmanli, *JACS* **72**, 965 (1950).

[52] Meerwein, Buchner, and Emster, *J. prakt. Chem.* **152**, 237 (1939); Bergmann, Weizman, and Schapiro, *J. Org. Chem.* **9**, 408 (1944). See also Müller, *Angew. Chem.* **61**, 179 (1949).

[53] Mathur *et al.*, *J. Indian Chem. Soc.* **24**, 123 (1947); *et sequa*; Koelsch *et al.*, *JACS* **65**, 57 (1943); **66**, 412 (1944).

[54] Hodgson and Dodgson, *JCS* 870 (**1948**); *J. Soc. Dyers Colourists* **64**, 65 (1948).

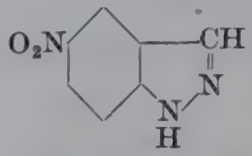
[55] Ladenburg, *Ber.* **9**, 219 (1876); Damschroder and Peterson, *Org. Syntheses* **20**, 16 (1940).

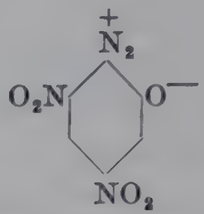
[56] Noelting, *Ber.* **37**, 2584 (1904).

[57] Porter and Peterson, *Org. Syntheses* **20**, 73 (1940).

group on an adjacent group is the decomposition of diazotized picramide, which is stable only in strong acid solution, and forms the diazo oxide (VIII) on treatment with water.

(VII)





(VIII)

Waters and his collaborators have studied the reactions of diazonium salts with special reference to decomposition and addition processes involving free radicals.[58] Waters classifies decomposition reactions of the aromatic diazo compounds into three types. (I) Decomposition in acid solution with formation of phenols:

$$ArN_2X + H_2O \longrightarrow ArOH + N_2 + HX.$$

This reaction is a decomposition of the diazonium cation, and the rate of evolution of nitrogen is independent of the nature of the anion X. (II) Nonionic decompositions of the aryldiazohydroxides.[59] (III) Reactions of the Sandmeyer and Gattermann type which occur in acid solution and need a copper catalyst; it is suggested that these are nonionic decompositions of diazonium cations, brought about by a single electron transfer from the catalyst:

$$ArN_2^+ + e \longrightarrow Ar + N_2$$

The appearance of azo compounds and polyaryls among the decomposition products of diazonium salts in aqueous solution near the neutral point in presence of a mild reducing agent indicates that in part diazo compounds can undergo decomposition of Type II.[60] Free aryl radicals are formed, which may, among other reactions, either (*a*) react with diazonium cations with single electron transfer from the reducing agent with formation of a symmetrical azo compound, or (*b*) attack undecomposed covalent diazo compounds with formation of a diazo biaryl compound, which eventually yields polyaryls or combines as in (*a*) to form an arylazobiaryl.[61] The theory of free-radical (or homolytic) reactions applies to the reactions of aromatic diazo compounds in nonionizing solvents and not to the ordinary reactions of diazonium salts in aqueous solution.[62]

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[58] Hanby and Waters, *JCS* 1792 (**1939**); and other papers; see also Waters, The Chemistry of Free Radicals, Clarendon Press, Oxford, 1946. A polarographic examination of diazotized amines has been recently carried out: Atkinson *et al.*, *JACS* **72**, 915 (1950).

[59] Cf. Hey *et al. JCS* 1799 (**1934**); *et sequa.*

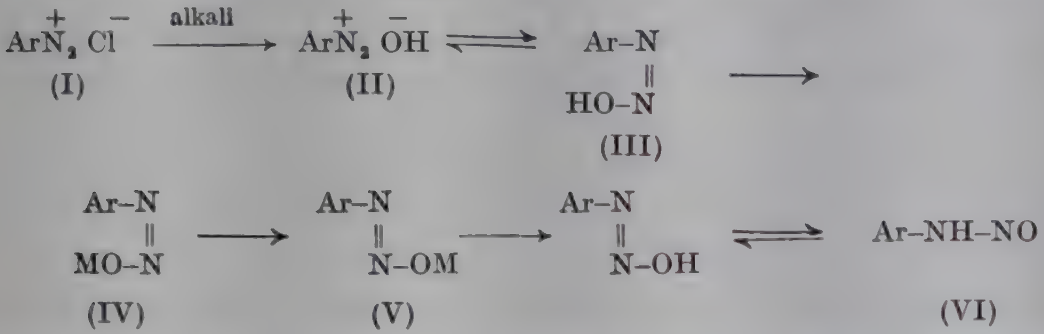
[60] Waters, *ibid.* 266 (**1942**).

[61] Saunders and Waters, *ibid.* 1154 (**1946**).

[62] Hey and Waters, *Chem. Revs.* **21**, 169 (1937); *JCS* 882 (**1948**); Contrast Hodgson, *J. Soc. Dyers Colourists* **64**, 99 (1948).

The action of alkali on diazonium salts is complicated. It is important from the dye chemist's point of view, and must be borne in mind in coupling reactions with phenols. It also provides a valuable method for preparation of diazo compounds in a stabilized solid form.

When a diazonium salt solution (I) is treated with an alkali, a strongly alkaline solution of a diazonium hydroxide (II) is first obtained; but the electrical conductivity falls rapidly, and isomerization to the alkali diazotate



$$\underset{\text{(I)}}{\mathrm{Ar\overset{+}{N}_2\,\overset{-}{Cl}}} \xrightarrow{\text{alkali}} \underset{\text{(II)}}{\mathrm{Ar\overset{+}{N}_2\,\overset{-}{O}H}} \rightleftharpoons \underset{\text{(III)}}{\begin{matrix}\mathrm{Ar{-}N}\\ \|\\ \mathrm{HO{-}N}\end{matrix}} \longrightarrow$$

$$\underset{\text{(IV)}}{\begin{matrix}\mathrm{Ar{-}N}\\ \|\\ \mathrm{MO{-}N}\end{matrix}} \longrightarrow \underset{\text{(V)}}{\begin{matrix}\mathrm{Ar{-}N}\\ \|\\ \mathrm{N{-}OM}\end{matrix}} \longrightarrow \begin{matrix}\mathrm{Ar{-}N}\\ \|\\ \mathrm{N{-}OH}\end{matrix} \rightleftharpoons \underset{\text{(VI)}}{\mathrm{Ar{-}NH{-}NO}}$$

(IV) of the weak aryldiazoic acid (III) takes place. The acid (III) resembles nitrous acid in its structure and degree of acidity. It cannot be isolated, since treatment of the alkali salt (IV) even with a weak organic acid leads to the diazonium salt. The alkali diazotate exhibits geometrical isomerism (Hantzsch); the *syn*-diazotate (IV) formed first is the reactive form, e.g., in diazo coupling. The *syn*-diazotate (IV) soon changes, especially in presence of excess alkali or when warmed, to the stable *anti*-diazotate (V), which may be isolated in solid form and stored more or less indefinitely under suitable conditions. Careful treatment of (V) with acetic acid results in a new and reversible isomerization, by which the nitrosoamine or *N*-nitroso compound (VI) is formed. Hantzsch's view of the geometrical isomerism of the diazotates is generally, but not universally, accepted.[63] Angeli[64] has suggested that the ability of diazo hydroxides to oxidize alcohol to aldehyde and hydroquinone to quinone is due to their functioning as *N*-oxides. The close relationship of all these compounds and their tautomeric character are indicated by the fact that by treatment with mineral acid the diazonium salt is regenerated.

The rate of decomposition of diazonium salts under alkaline conditions is an important factor in the manufacture of azo dyes; Oddo and Indovina[65] have determined the decomposition velocities of a series of diazotized amines in presence of different concentrations of caustic soda.

Diazotized *p*-nitroaniline gives with caustic soda solution in presence of ammonium salts a red color which is a sensitive test for them.[66]

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[63] See also Grachev *et al.*, *J. Gen. Chem. U.S.S.R.*, **18,** 1179 (1948); and earlier papers.

[64] Angeli, *Ber.* **62,** 1924 (1929).

[65] Oddo *et al.*, *Gazz. chim. ital.* **65,** 939 (1935).

[66] Riegler, 1897; Feigl, *Mikrochemie*, **13,** 129 (1933).

Estimation of diazonium salts. The usual method by which diazonium salts are estimated is titration against a suitable coupling component such as alkaline β-naphthol. The diazonium salt solution is kept in an amber-colored burette provided with a jacket through which ice water is circulated to avoid decomposition by light and heat. The coupling component is taken in a glass stoppered bottle; after each addition of diazonium salt the bottle is stoppered and rapidly shaken. The end point is determined by placing a drop of the mixture on filter paper and observing the development of color on spotting with a drop of diazonium solution; when the end point has been overstepped, color develops on spotting with a solution of a coupling component, R-salt being customarily used. Intermediates which couple readily with diazonium salts can be estimated by the same reaction. Examples of such intermediates are *m*-phenylenediamine, naphthols (including the Naphtol AS type), naphthylamines, aminonaphthols and their sulfonic acids; amines are dissolved in hydrochloric acid and phenols in caustic soda solution, sodium acetate being added for pH control. A relatively stable diazonium salt is chosen, e.g., diazotized *p*-nitroaniline, 2,5-dichloroaniline, or 5-nitro-*o*-anisidine (Red B). If the intermediate being estimated is a sulfonic acid so that a soluble dye results from the titration, the dye is salted out from time to time prior to the spot test so that the color of the dye does not interfere.

Slow-coupling diazonium salts such as 1-diazo-2-naphthol-4-sulfonic acid and its 6-nitro derivative cannot be estimated by the coupling method. The technically important 1-diazo-2-naphthol-4-sulfonic acid liberates nitrogen quantitatively and immediately on treatment with sodium arsenite, and can be estimated in this manner.[67] Following the suggestion of Schmidt and Maier[68] that decomposition of the diazo compound could be effected by sunlight and the evolved nitrogen measured, Spencer and Taylor[69] have found that the decomposition can be effected smoothly by the light from an ordinary carbon arc lamp, and they have developed an apparatus and technique by which a method that is rapid, accurate, and of wide applicability for the estimation of diazo compounds has become available.

STABILIZED DIAZONIUM SALTS

The production of azoic dyes (Chapter XXII) on the fiber by impregnation with the anilide of 2-hydroxy-3-naphthoic acid or an analogous coupling component and development with a diazonium salt has been facilitated by the introduction of stabilized diazonium salts, so that the dyer or printer does not need to carry out the process of diazotization. Nitrosamine Red, the *anti*-diazoate of *p*-nitroaniline, was marketed by BASF as long ago as 1893 for use in the production of Para Red (1-*p*-nitrobenzeneazo-2-naphthol, produced on the fiber). With the introduction of Naphtol AS and its analogs from 1920, a series of primary amines, specially suitable for application in azoic dyeing and printing, have been introduced to meet the demand for a full range of shades with the requisite fastness. Apart from the difficulties encountered in diazotization of some of these amines, the rapid expansion in the utilization of the azoic colors created a growing need for simplified use of the amines, and stabilized diazonium salts are now manufactured on a large scale.

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[67] Ostroshinskaja, *Anilinokrasochnaya Prom.* **4**, 368 (1934).

[68] Schmidt and Maier, *Ber.* **64**, 767 (1931).

[69] Spencer and Taylor, *J. Soc. Dyers Colourists* **63**, 394 (1947).

Classification of stabilized diazo compounds. The commercial stabilized diazo compounds can be classified into two groups: (A) diazonium salts stabilized under acid conditions, which exhibit diazonium salt reactions (e.g., coupling) immediately when dissolved in water; and (B) diazo compounds which are stable under alkaline conditions and which undergo the coupling reaction after acidification or special treatments such as steaming. The two groups would also represent a broad classification based on stabilization for (A) use in developing textile materials which have been impregnated or printed with an alkaline solution of a " naphthol "; and (B) the preparation of printing compositions by admixture with the alkali salts of " naphthols " of the Naphtol AS type. The Fast Salts of the IG and other manufacturers belong to the first group; and the diazo compounds of the second group used in printing compositions were marketed by the IG under the names of Rapid Fast, Rapidogen, and Rapidazol printing colors. The Fast Salts are standardized at a definite (e.g., 20%) diazonium salt content. Examining a series of Fast Salts, Moualim[70] found that the average diazonium salt content, determined by titration with alkaline β-naphthol and calculated as aryldiazonium chloride, was 22–24%; the most commonly encountered inorganic constituents, employed as stabilizers and diluents, were zinc chloride, magnesium chloride and sulfate, aluminium sulfate, and common salt.

There is an extensive patent literature on processes for the stabilization of diazonium salts and diazo compounds, but they largely represent differences in detail. Each of the two groups into which the stabilized diazo compounds have been classified can be further divided into three main types. The diazonium salts are usually stabilized in the form of (*a*) diazonium sulfates; (*b*) double salts; or (*c*) arylsulfonates; and the diazo compounds for use in printing compositions are in the form of (1) *anti*-diazotates; (2) diazoamino compounds, or (3) diazosulfonates. The applicability of the methods available for stabilization in one or other of these forms is limited by the nature of the amine; a few typical amines which are amenable to stabilization by the given method are mentioned below.[71]

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[70] Moualim, unpublished work.

Diazonium sulfates and chlorides. Diazonium salts are more stable in increasingly acid media, and a generally applicable method involves isolation in the form of the diazonium sulfates in presence of free sulfuric acid. Azophor Red (MLB), an early representative of this type, was prepared by diazotization of *p*-nitroaniline in presence of excess sulfuric acid, concentration of the solution under reduced pressure at about 40°, and conversion into a powder by admixture with anhydrous sodium sulfate. Azophor Blue D was a similar product from dianisidine. Nitrazol C was prepared by diazotization of *p*-nitroaniline in concentrated sulfuric acid, partial neutralization with magnesium oxide and then admixture with sodium sulfate. The diazotization can be carried out in strong sulfuric acid solution with nitrosylsulfuric acid, and the diazonium salt precipitated by the addition of alcohol or other solvent miscible with sulfuric acid;[72] the temperature should be kept below 0°. Among the amines which can be treated by this method are the nitroanilines, chloroanilines, aminophenyl ethers and their halogenated derivatives, and monoacyl *p*-phenylenediamines. The diazonium salts from amines of the type of 4-phenoxyacetamido-2,5-diethoxyaniline and halogenated 4-aminodiphenyl ethers can be simply salted out from the diazotization solution.[73] Similarly 4-amino-4′-methoxydiphenylamine (Variamine Blue B Base) is diazotized by means of hydrochloric acid and sodium nitrite, but with the addition of an equivalent of sulfuric acid which facilitates smooth diazotization; the diazonium chloride is then salted out. 8-Amino-1-anilino-2-naphthols yield diazonium chlorides which are stable in dry form, and give brown shades with arylides of 2-naphthol-3-carboxylic acid.[74]

The stabilization of diazonium salts is facilitated by diazotization in presence of amides such as butyl- or dimethylformamide or acetylmorpholine.[75]

Double salts. The zinc chloride double salts are the commonest, but other metal salts (e.g., manganous salts)[76] and salts of complex acids have been suggested in patents and a few find limited application. Among such complex salts are borofluorides, fluotungstates, and flualuminates. The double salt method is specially applicable to the aminoanthraquinones, aminoazobenzenes, and benzidine derivatives.

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[71] See also *BIOS* 988.

[72] IG, BP 441,085; Schnitzspahn, DRP 622,306.

[73] Ciba, BP 434,158; IG, BP 440,964.

[74] du Pont, BP 531,625.

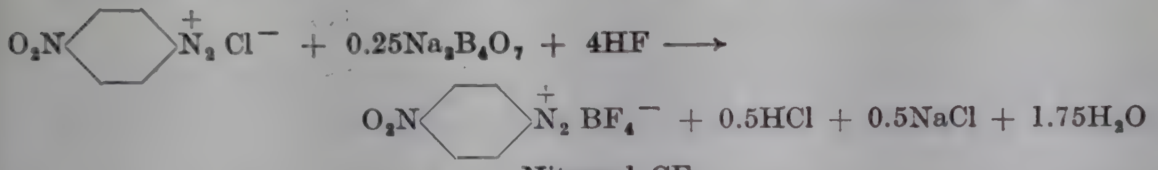
[75] Lubs and du Pont, USP 2,209,985.

[76] Ciba, BP 476,143.

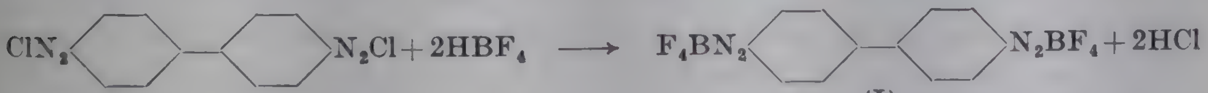
Zinc chloride double salts are prepared easily. When a solution of zinc chloride, in slight excess over the quantity theoretically required for the double salt $[(ArN_2Cl)_2\ ZnCl_2]$, is added to a solution of the diazonium chloride (e.g., from α-aminoanthraquinone), the double salt usually crystallizes, the separation being completed by the addition of common salt.

Zinc chloride double salts are further stabilized by the addition of sulfamic acid (about 10%), and the printing pastes then have improved keeping qualities.[77] Aliphatic sulfonic acids and their soluble salts are also stabilizing agents.[77a] Stabilized diazonium salts are made nondusting by mixing with diethyl carbonate.[77b]

Nitrazol CF, as made by the IG, is the borofluoride prepared by treatment of the diazonium chloride with borax and hydrofluoric acid.[78] Diazotized *m*-chloroaniline (Fast Orange Salt GC) is also stabilized as the borofluoride. Diphenyl-4,4′-bis-diazonium borofluoride (I; dec. 135-137°) is prepared by addition of 40% fluoboric acid (commercially available, or obtainable by dissolving boric acid in 60% hydrofluoric acid) to a solution of tetrazotized benzidine below 10°. A thick paste of (I) forms and the product is filtered, washed with methanol and ether, and dried *in vacuo* over sulfuric acid.[79]

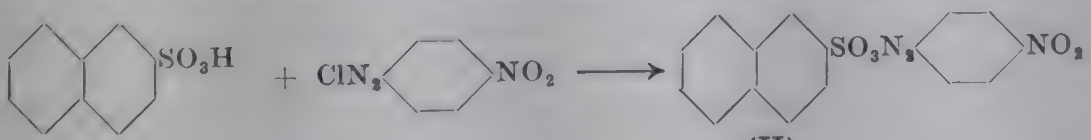

O₂N
N₂ Cl⁻ + 0.25Na₂B₄O₇ + 4HF
O₂N
N₂ BF₄⁻ + 0.5HCl + 0.5NaCl + 1.75H₂O

Nitrazol CF



(I)

Arylsulfonates. These are the diazonium salts of aromatic sulfonic acids, and an early German product of this class was Paranil A (II), prepared by condensation of diazotized *p*-nitroaniline with naphthalene-β-sulfonic acid in acid solution. The reaction



(II)

$$ArN_2Cl + Ar'SO_3H \rightleftharpoons ArN_2SO_3Ar' + HCl$$

(III)

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[77] Clark, USP 2,314,196.

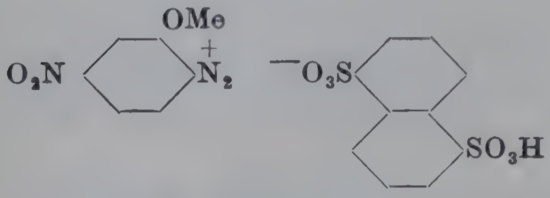
[77a] Glahn, Walsh, Streck, and General Aniline and Film, USP 2,381,145.

[77b] Bergstrom and General Aniline and Film, USP 2,477,165.

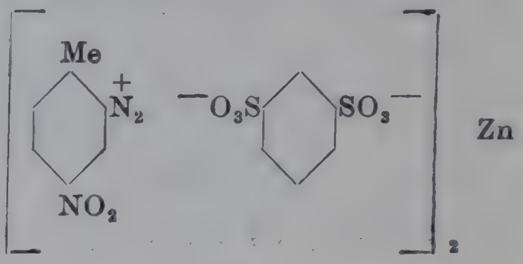
[78] *BIOS* **1149.**

[79] Schiemann and Winkelmüller, *OSCV* II, p. 188.

is reversible, the isolation of (III) being possible if it is sparingly soluble and can be salted out. When the diazonium arylsulfonates are dissolved in water, they undergo hydrolysis to the diazonium hydroxide and ionization, and couple readily. An example of a commercial diazonium arylsulfonate is Fast Red Salt B (IV). It is prepared by diazotization of the amine in the normal manner (a temperature of 15–20° being permissible), clarification of the diazonium solution by means of decolorizing carbon and kieselguhr, and conversion of the diazonium chloride into (IV) by addition of a little over one mole of naphthalene-1,5-disulfonic acid and the calculated amount of caustic soda solution. On being cooled to 5° for a few hours (IV) crystallizes, and is filtered on a centrifuge. Dried at 55-60° in a current of air, it is neutralized and standardized by admixture with magnesium oxide and alumina.



(IV)



(V)

Suitable sulfonic acids are naphthalenemono- and polysulfonic acids, *N*-acetylsulfanilic acid, and sulfobenzoic acid. Sulfobenzoates and sulfosalicylates are easy to prepare and dehydrate.[80] The IG find benzenesulfonates adequate for diazotized 4-aminobenzonitrile containing substituents in the 2,5-positions.[81] Diazonium arylsulfonates, in which the arylsulfonic acid residue contains a carboxyl or second sulfonic group, can be isolated as the zinc salt (e.g., V).[82]

The decomposition of diazonium salts in aqueous solution is retarded by arylsulfonic acids, and the keeping qualities of diazonium salt solutions can be increased in this manner. The stabilizing effect on a given diazonium salt depends on the nature of the arylsulfonic acid and its molar proportion, the pH, and the temperature.[83]

When *p*-nitrobenzenediazonium chloride reacts with sodium 2-naphthol-1-sulfonate, the product is the naphthylsulfonate (VI), which by acid or heat treatment forms *p*-nitrobenzeneazo-β-naphthol (Para Red). Rowe[84] has shown in a long series of papers that the action of caustic soda on (VI) and its analogs is complicated, and products such as the dihydrophthalazine

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[80] Frahm, *Chem. Weekblad.* **37,** 238 (1940).

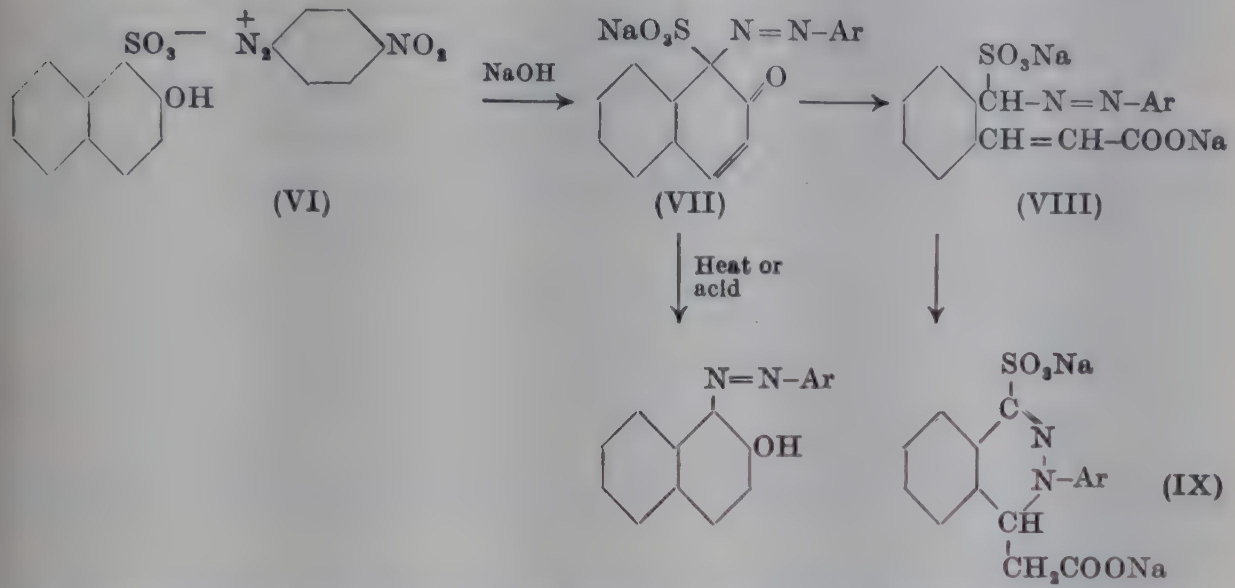
[81] IG, BP 512,798.

[82] Markush, Mayzner, and Pharma-Chemical Corp., USP 2,237,885.

[83] Marriott, *J. Soc. Dyers Colourists* **52,** 172 (1936).

[84] Rowe *et al. JCS* 690 (**1926**); *et sequa*; *ibid.* 829 (**1947**).

(IX) are formed, through the intermediate stages of the hemiquinone (VII) and the cinnamic acid derivative (VIII). An interesting and unusual fission of the naphthalene ring is involved.



(VI) (VII) (VIII) (IX)

Large-scale production of solid diazonium salts. The explosive and inflammable character of the diazonium salts is a factor requiring careful consideration in the manufacture of the Fast Salts. The hazard is in the drying and grinding stages. The drying procedure at the Offenbach factory of the IG, the largest producer of Fast Salts in the pre-war years, has been stated to be unsatisfactory.[85] Simple equipment, consisting of tray dryers operated at 50° and provided with safety flaps in case of explosion, was employed, with the object of cutting down the loss by damage to the plant, since occasional mishaps were unavoidable. During grinding of Fast Salts with Glauber salt, aluminium sulfate, etc., dry ice (solid carbon dioxide) was added. The initial size reduction of Fast Salts was carried out in disintegrators made of phosphor bronze to minimize the danger of self-ignition and explosion. After dilution with dry inorganic salts, Fast Salts could be ground in iron mixers consisting of revolving drums, provided with scraper blades. Each mixer was 1 to 3 tons in capacity. The plant was provided with a very good dust-extracting system.

STABILIZED DIAZO COMPOUNDS FOR PRINTING COMPOSITIONS

Anti-diazotates. When a diazonium salt solution is treated with strong (50%) alkali and the mixture is heated, a stable alkali salt of the aryldiazo hydroxide, also regarded as the nitrosoamine, separates. This procedure is the simplest by which a stable diazo compound, suitable for mixing with an alkaline salt of a "naphthol," can be prepared. The composition of the Rapid Fast colors of the IG, which were such mixtures of alkali naphtholates and *anti*-diazotates or nitrosoamines, is stated in Chapter XXII. The mixtures possess the necessary stability for storage in paste or powder form, and are used for textile printing after making up with suitable thickeners such as starch.

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[85] *BIOS* 1363.

The usual experimental procedure for preparation of an *anti*-diazotate (or nitrosoamine) is to diazotize the amine under suitable conditions and convert the diazonium chloride or sulfate into the potassium or sodium *syn*-diazotate by addition of the diazonium solution to a solution of potassium or sodium hydroxide (amount calculated for neutralization of the acid and formation of the alkali diazotate) at about 0°; after 2–3 hours the *syn*-diazotate solution is slowly added to 50–70% caustic alkali solution at 100–125°. When a test with β-naphthol shows that the diazotate no longer couples, an indication of complete conversion to the *anti*-form, the reaction mixture is diluted with water until it forms a clear solution at about 75°. When cooled slowly to 20° the alkali *anti*-diazotate crystallizes and is filterable.

Diazoamino compounds. When a diazonium salt reacts with a primary or secondary amine under neutral or weakly acid conditions, a diazoamino compound (I) is formed:

$$ArN_2Cl + R\text{–}NH\text{–}R' \longrightarrow Ar\text{–}N{=}N\text{–}NRR' \qquad (I)$$

With aromatic amines both *N*-coupling and *C*-coupling can take place, and formation of the diazoamino compound, rather than of the aminoazo compound, depends not merely on the pH of the reaction mixture, but also on the nature of the diazonium salt and of the amine (see Chapter XI). The triazene derivative (I) is readily decomposed by mineral acid at low temperature or by organic acids at higher temperatures, the diazonium salt being regenerated. If the amine R-NH-R[86] contains a sulfonic or carboxyl group, the diazoamino compound (I) is rendered alkali-soluble, and the alkali salts form stable mixtures with alkali "naphtholates." Such mixtures were marketed by the IG as Rapidogen colors, and they are listed, together with their composition, in Chapter XXII. When a Rapidogen is pasted up and printed and the fabric is dried, no coupling takes place; but on acid treatment, usually with acetic acid and formic acid in a special "acid steamer," the azoic dye is formed.

The preparation of the diazoamino compound is simple. The amino acid is dissolved in sodium carbonate solution, the diazonium salt solution is run in at about 10°, and the diazoamino compound, usually yellow, salted out. In a typical procedure[86] for the preparation of a diazoamino compound for use in printing compositions, the base (Blue RR; 4-benzamido-

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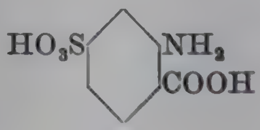
[86] For an account of the IG method of preparation of such diazoamino compounds, see *BIOS* 988.

2,5-dimethoxyaniline; 1 part) is diazotized by means of sodium nitrite (1), 30% hydrochloric acid (5), and water (20) at 10°. The diazonium solution is clarified, filtered, and added with stirring to a solution of *N*-methyltaurine (1.1), soda ash (4), and salt (6) in the minimum amount of water. After storage overnight the diazoamino compound is filtered and dried at 80° at reduced pressure (yield 90%).

Both aliphatic and aromatic amino acids are employed for the stabilization of diazonium salts as diazoamino compounds, the most generally used amino acids being sarcosine (II), *N*-methyltaurine (III), sulfoanthranilic acid (IV), and 2-methyl(or ethyl)amino-5-sulfobenzoic acid (V). Aliphatic amino acids are unsuitable for negatively substituted diazonium salts, since the diazoamino compounds are not readily decomposed by acid.

(II) CH_3NHCH_2COOH

(III) $CH_3NHCH_2CH_2SO_3H$



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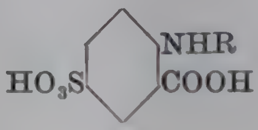

(V)

Varied types of aliphatic, aromatic, and heterocyclic amines carrying carboxyl, sulfonic, and hydroxyl groups for imparting solubility have been suggested in the patent literature for the condensation with diazonium salts to produce diazoamino compounds. Glucamines,[87] cyanamide,[88] ethanolamines,[89] furfurylaminoacetic acid,[90] salts of sulfoanthranilic acid and volatile organic bases,[91] sulfatoethyl ethers of aminophenols [e.g., 1,2,4-$NHMe\text{-}C_6H_3(OCH_2CH_2\text{-}OSO_3Na)_2$],[92] proline, and piperidine carboxylic and sulfonic acids[93] are examples. Calco prepare diazoamino compounds from *N*-nitro- or *N*-sulfoguanylurea[94] and from *p*-guanidylbenzenesulfonic acid, $H_2N\text{-}C(=NH)\text{-}NHC_6H_4SO_3H$.[95] Special stability is claimed[96] for the *bis*-diazoamino compounds from diiminodicarboxylic acids such as ethylene diimino diacetic acid, $HOOC\text{-}CH_2\text{-}NH\text{-}CH_2\text{-}CH_2\text{-}NH\text{-}CH_2\text{-}COOH$.

Diazonium salts can be condensed with amines, such as $H_2N\text{-}C_6H_4\text{-}SO_2NHCH_2CH_2OH$, in which alkali-solubility is secured by a sulfonamide group.[97] Soluble diazoamino compounds of the type $Ar\text{-}N=N\text{-}NR\text{-}SO_3Na$, in which R is an alkyl group, are obtained by treatment of sodium alkyl sulfamate dissolved in a neutral medium with a diazonium salt.[98] The IG have described the preparation of water-soluble diazoamino compounds of aminoazo compounds by coupling a diazonium salt with a diazoamino compound from diazotized 2,5-dimethoxyaniline and sarcosine.[99] The interaction of nitrosyl chloride with about two molar proportions of an arylamine leads to the diazoamino compounds;[100] water-insoluble diazoamino compounds prepared by such methods can be dissolved in organic solvents and emulsified with aqueous solutions of the alkali "naphtholates."

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[87] du Pont, BP 429,618.

[88] IG, BP 443,222.

[89] Heaton, BP 457,763; 463,515.

[90] du Pont, BP 479,848; 481,019.

[91] IG, BP 480,169.

[92] Kern, USP 2,190,841.

[93] Dahlen and du Pont, USP 2,008,750; 2,021,911; Markush and Pharma-Chemical Corp., USP 1,982,681; 1,986,276.

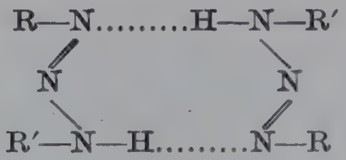
[94] Calco, BP 515,980.

[95] Lecher, Adams, Orem, and American Cyanamid, USP 2,200,926.

[96] Markush, Mayzner, Miller, and Pharma-Chemical Corp., USP 2,110,270.

[97] Maynard, Wiest and du Pont, USP 2,416,187.

Diazoamino compounds are associated in solution, and the dimeric form (VI) is regarded by Hunter[101] as the most probable type of cyclic polymer on stereochemical grounds. The weak salt-forming properties



(VI)

of diazoamino compounds are due to the electron-donor character of the azo nitrogen atoms, combination with one or two equivalents of acid (one or two protons) being demonstrable. The salts (especially VII in view of the adjacent charge rule) are very unstable, and break down into a mixture of diazonium salts and amines. The ions from a diazoamino compound functioning as a monacid or diacid base are resonance hybrids. The

$$\text{R–}\overset{+}{\text{N}}\text{H=N–NH–R}' \longleftrightarrow \text{R–NH–N=}\overset{+}{\text{N}}\text{H–R}'$$

$$\text{R–}\overset{+}{\text{N}}\text{H=}\overset{+}{\text{N}}\text{H–NH–R}' \longleftrightarrow \text{R–NH–}\overset{+}{\text{N}}\text{H=}\overset{+}{\text{N}}\text{H–R}' \qquad \text{(VII)}$$

proportion of the diazonium salts $R\overset{+}{N}_2$ and $R'\overset{+}{N}_2$ formed on decomposition by mineral acid depends on the nature of the nuclear substituents in R and R′ if both R and R′ are aromatic groups; the predominant resonance structure of the diazoamino compound will be that in which the imino group is attached to the more electronegatively substituted aromatic radical, and a correspondingly larger amount of the diazonium salt of the other aromatic radical is formed on decomposition. When R or R′ is aliphatic, as in most of the stabilized diazo compounds of commerce belonging to the diazoamino type, the aryldiazonium salt is quantitatively formed by the action of acid and couples immediately with the second component with which it is admixed before acid treatment.

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[98] Zavel'skî, RP 66,323.

[99] IG, BP 465,484.

[100] Mayer and Solvay Process Co., USP 2,133,037; Interchem Corp., BP 552,919; USP 2,309,946; 2,310,012–3.

[101] Hunter, *JCS* 323 (1937).

Diazosulfonates.[102] Schmitt and Glutz in 1869 observed the formation of diazosulfonates (I) by the action of sodium sulfite on diazotized *p*-aminophenol, and Fischer in 1878 prepared several aryldiazosulfonates as intermediate products in the reduction of diazonium salts to arylhydrazines. Hantzsch isolated two groups of diazosulfonates and diazocyanides, which he regarded as geometrical isomers corresponding to normal (*syn*) and iso (*anti*) diazotates. Hodgson[103] has recently revived Bamberger's suggestion that Hantzsch's *syn*- and *anti*-diazo compounds, including the diazocyanides, diazosulfonates, and alkali diazotates, are structural and not steric isomers, but there is no doubt regarding the correctness of Hantzsch's view. The *syn*- and *anti*-structure of the diazocyanides has found support in investigations of their infrared spectra, magnetic optical rotatory powers, and diamagnetic susceptibilities.[104]

$$\mathrm{ArN_2Cl + Na_2SO_3 \longrightarrow \underset{(I)}{Ar{-}N{=}N{-}SO_3Na} + NaCl}$$

Hantzsch found that of the two isomeric diazosulfonates only the unstable or *syn*- form couples with β-naphthol. The *syn*-compound also reacts with iodine according to equation (1), and the conversion of the *syn*- into the *anti*-diazosulfonate can be quantitatively followed by titration with iodine. Hantzsch and Schmiedel[105] showed that nuclear substituents influenced the stability of the *syn*-compounds and the rate of conversion into the *anti*-form. Thus alkyl groups made the *syn*-form more labile, *o*-halogenated diazonium salts gave more stable *syn*-compounds than the *m*- and *p*-derivatives, and diazotized *p*-nitroaniline did not yield the *syn*-diazosulfonate because of its immediate conversion into the *anti*-form.

$$\mathrm{Ar{-}N{=}N{-}SO_3Na + H_2O + I_2 \longrightarrow ArN_2SO_4H + NaI + HI} \qquad (1)$$

Stabilization of diazonium salts as the diazosulfonates is a useful technical process for diazonium salts which are not amenable to treatment by the two methods described earlier. Thus the diazonium salts of *p*-aminodiphenylamine and its derivatives undergo decomposition with alkali and cannot be converted into the alkali diazotates; likewise their tendency for decomposition and their very slow reactivity as diazonium salts render them unsuitable for condensation with amines to form diazoamino compounds. With neutral sulfite, however, they readily form diazosulfonates, which are stable under alkaline conditions, so that they can be mixed with alkali "naphtholates" and applied in textile printing. The important Fast Base, Variamine Blue B (II, see Chapter XXII), is conveniently stabilized by this method. Monoacyl-*p*-phenylenediamine derivatives (e.g., Blue BB, III) also yield stable diazosulfonates. Development of the print, i.e., azoic coupling, takes place on steaming, when the *anti*-diazosulfonate is converted into the *syn*-form ; but coupling is more effectively carried out by oxidation of the diazosulfonate to the aryldiazonium sulfate by means of neutral sodium chromate. The oxidizing agent is incorporated in the printing paste, and the print is then submitted to the usual ageing or steaming treatment. Many *anti*-diazosulfonates are converted into the active *syn*-form on exposure to light, and mixtures with coupling components can be developed in this manner for the production of photographic prints.[106]

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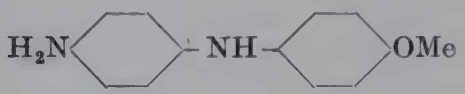
[102] For an account of diazosulfonates in textile printing, see Desai, Mehta, and Thosar, *J. Soc. Dyers Colourists* **54**, 371 (1938).

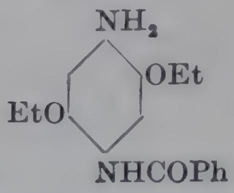
[103] Hodgson, *JCS* 470 (**1943**); 207 (**1945**).

[104] Sheppard and Sutherland; Anderson, Bedwell and Le Févre, *JCS* 453, 457 (**1947**); *Chemistry and Industry* 158 (**1948**); contrast Hodgson and Marsden, *JCS* 395 (**1944**).

[105] Hantzsch and Schmiedel, *Ber.* **30**, 71 (1897).

(II)





(III)

A few mixtures of diazosulfonates and sodium salts of the members of the Naphtol AS series have been marketed by the IG under the name of Rapidazols. The range has so far been limited to mixtures yielding blue and black shades.

Desai, Mehta, and Thosar[102] have studied the preparation and properties of diazosulfonates derived from some of the aromatic amines (" Fast Bases ") usually employed for diazotization and coupling with members of the Naphtol AS series, the application of the diazosulfonates in textile and photographic printing, and the rates of conversion of the *anti*- into the *syn*-compounds.

Miscellaneous methods. In addition to these three methods which are used in current technical practice for the preparation of azoic printing compositions, other procedures have been described in the patent literature. Examples are mixtures of "naphthol," primary amine, and nitrite with various additions for bringing about diazotization and coupling at the desired stage; mixtures containing a Schiff's base and sodium nitrite;[107] and mixtures containing an arylhydrazinesulfonic acid, the development of which is carried out by oxidation.[108] Aqueous solutions of the diazonium and coupling components can be stabilized by means of quaternary ammonium bases containing at least one hydroxyethyl group.[109] A printing composition which does not require to be steamed for development consists of a mixture of a "naphthol," *m*-aminobenzenesulfonanilide, sodium nitrite, caustic soda and sodium sulfate. Since both "naphthol" and diazo component are soluble in aqueous caustic soda, the printed fabric has merely to be padded cold with aqueous acetic acid, when diazotization and coupling take place immediately.[110]

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[106] St. Denis, BP 440,144.

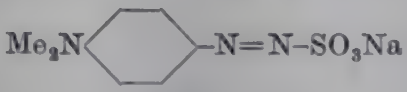
[102] See p. 231.

[107] Kuhlmann, BP 459,766.

[108] St. Denis, BP 457,718.

[109] Lecher, Parker, and American Cyanamid, USP 2,214,559; see also Markush, Miller, and Pharma-Chemical Corp., USP 2,105,326.

The diazosulfonate (IV), obtained by treatment of diazotized *p*-aminodimethylaniline with sodium bisulfite, is a rodenticide used in 0.1% concentration in grain.


(IV)

PHOTOCHEMISTRY OF DIAZO COMPOUNDS

Diazo compounds in general are sensitive to light. Diazonium salts undergo photochemical decomposition with evolution of nitrogen, the quantitative effect depending on the nature of the diazonium salt, as in the action of heat, but in a roughly reverse order. Photochemical isomerization between the *syn*- and *anti*-forms of the metallic diazotates, diazocyanides, and diazosulfonates has also been observed, and both these effects of decomposition and isomerization have found practical application.

The first quantitative study of the action of sunlight on diazonium salts was made by Ruff and Stein[111] in 1901. Using their results Spencer[112] calculated the relative units of time required for total destruction of the diazonium salts derived from a series of amines. The values varied from 29 units for diaminofluorene to 75 for benzidine, 125 for *p*-nitroaniline, and 200 for *o*- and *p*-toluidine. Ljaschenko and Kirner[113] exposed diazonium salt solutions at 0° in glass and quartz vessels to light from a mercury vapor lamp, and measured the nitrogen evolved in 3 hours. The figures showed that the rates of decomposition were more or less in the inverse order of Snow's results[34] for the decomposition of diazonium salts by heat. The diazonium salts of negatively substituted amines exhibiting comparatively high stability to heat were rapidly decomposed by ultraviolet light; conversely, diazotized aniline and the toluidines were relatively stable to light. Measuring the decomposition similarly, Schmidt and Maier[114] determined the stability of the mercurous, ferric, cadmium and zinc chloride double salts of diazonium salts of *p*-phenylenediamine derivatives of the type used in photography. 1-Diazo-2-naphthol-4-sulfonic acid and diazotized *p*-aminodiphenylamine, two other diazonium salts of practical interest, have been studied by Schröter,[115] who found that the quantum yield was independent of other conditions, such as temperature and concentration, within wide limits. Light of wave length 4,000–4,500A, especially 4,050A and 4,360A (the mercury lines), is the most effective.[116]

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[110] Sandoz, BP 517,030.

[111] Ruff and Stein, *Ber.* **34,** 1668 (1901).

[112] Spencer, *Phot. J.* **68,** 490 (1928).

[113] Ljaschenko and Kirner, *Anilinokrasochnaya Prom.* **4,** 272 (1934).

[34] See p. 217.

[114] Schmidt and Maier, see ref. 68; see also *J. prakt. Chem.* ii, **132,** 153 (1932).

Diazo Photographs and Prints

The action of light on diazo compounds can be utilized for production of photographs and photographic prints, both positive and negative, on paper, plastic films, and textiles. Green, Cross, and Bevan[117] described a process of photoprinting on cotton fabrics by dyeing with Primuline, diazotizing on the fiber, exposing to light under a stencil, and developing the residual undecomposed diazonium salt with alkaline β-naphthol. Later attempts to utilize such methods in textile printing have not proved technically successful,[117a] but diazotype papers and films are largely used; and for the reproduction of engineering drawings and similar purposes diazo prints are now preferred to the older and much more tedious blue-print process.

The diazonium salt can be applied to the paper or film and, after exposure, the print developed by coupling; or as in printing the Rapid Fast and other compositions the paper can be coated with a composition containing both the diazonium salt and the coupling component. In the first method diazonium salts (stabilized as zinc chloride double salts, etc.) of *p*-aminodiphenylamine, *p*-aminodimethylaniline and monoacyl-*p*-phenylenediamine derivatives (e.g., 4-benzamido-2,5-diethoxyaniline or Blue BB Base) are mainly employed. Numerous other diazonium salts, mostly derivatives of *p*-phenylenediamine, have been mentioned in the patent literature as being suitable for the diazotype process; e.g., the diazonium compounds prepared from *N*-4-amino-2,5-dibutoxyphenyl methyl carbamate;[118] *N*-4-Amino-3-methylphenyl-*N*-ethylglycineamide and similar compounds of the general formula 1,2,4-NH_2-C_6H_3X-NR-$(CH_2)_n$-R′; 1-*p*-aminophenylpyrollidine;[119] amines of the type of Blue BB in which the benzoyl group is replaced by other acid groups or by -CO-O-C_2H_4-OR;[120] 2,5-dialkoxy-4-aminoacetanilide in which the alkyl groups are isopropyl or contain more than four carbon atoms;[121] 4-carboalkoxyamino-2,5-dialkoxyanilines,[122] alkoxy- and dialkoxy-*p*-aminodiphenyls,[123] and hydrogenated heterocyclic bases fused to benzene rings containing an amino group.[124] " Diazotized " casein has been suggested as a suitable sensitizing agent; developed with H-acid and β-naphthylamine this gives a deep black image.[125]

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[115] Schröter, *Z. wiss. Phot.* **28,** 1 (1930); Eggert and Schröter, *Z. Elektrochem.* **34,** 602 (1928). See also Jonge and Dijkstra, *Rec. trav. chim.* **67,** 328 (1948).

[116] Horio *et al., J. Soc. Chem. Ind. Japan,* **34,** 367 (1931); **37,** 322 (1934); *Z. wiss. Phot.* **33,** 273 (1935).

[117] Green, Cross, and Bevan, *J. Soc. Chem. Ind.* **9,** 1001 (1890).

[117a] See, however, General Aniline and Film, BP 632,932.

[118] Jacobus and Bose, USP 2,326,782. See also Johnston, USP 2,456,514.

[119] Weissberger *et al.,* USP 2,336,309; 2,350,843.

[120] Murray, BP 532,958; Mason and Sons, and Norman, BP 539,031.

From an investigation of some 50 diazotized derivatives of aniline, Brown[126] concludes that the positive polar substituents (e.g., NR_2, NHCOPh, NHPh, OR), as well as heterocyclic types such as piperidino or morpholino groups in the *o*- or *p*- positions, are the best when high light sensitivity and good keeping properties are desired. Brown has also outlined the historical development of the diazotype process and the composition of modern coatings.[127]

Phloroglucinol and resorcinol are the main coupling components. Treatment with an aqueous alkaline solution of the phenol has presented various difficulties, such as danger of deterioration of the paper and discoloration of the whites, but these have been substantially eliminated. Careful pH control by incorporation of acidic constituents in the coated paper and by use of a diazonium salt (e.g., diazotized *p*-aminodiphenylamine and its derivatives) capable of coupling under faintly acid conditions are remedies for the problem of alkalinity. Discoloration of the whites can be avoided by addition of reducing agents to the developing bath[128] or by addition to the coupling solution of a nonvolatile acid and a volatile amine in excess of the acid to give $pH > 7$; a typical developing bath thus consists of resorcinol, diethylamine, and oxalic acid in water.[129]

Kalle and Co., a subsidiary of the IG, who have been primarily responsible for the development of this process, are large-scale manufacturers of diazo paper and films (" Ozalid " products), and the following account of Kalle chemicals and methods is based on a *BIOS* report[130] and on the writer's visit to the Kalle plant at Biebrich-Wiesbaden.

Typical formulae for the coating compositions and for the developers, as used by Kalle and Co., are appended: *Diazo coating compositions*: (*a*) Blue BB Salt (34.72 kg. corresponding to 23.96 kg. of 100%), naphthalene-1,3,6-trisulfonic acid (56.91 kg.), aluminium sulfate (12.90 kg.), boric acid

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[121] Leuch and Harding, Ltd., BP 521,492.

[122] Mason and Sons, and Norman, BP 489,214.

[123] Kalle and Co., BP 471,614.

[124] Kalle and Co., BP 467,145.

[125] Waterman and Borgenius, BP 473,244; *J. Soc. Dyers Colourists* **56**, 23 (1940).

[126] Brown, *Chemistry and Industry* **22,** 146 (1944).

[127] Brown, *J. Soc. Dyers Colourists* **60,** 186 (1944).

[128] Murray, BP 320,395; 320,603.

[129] Crowby and Mullen, USP 2,308,058.

[130] *BIOS* **772**; see also *BIOS* **435**; **1475**; *FIAT* **528**.

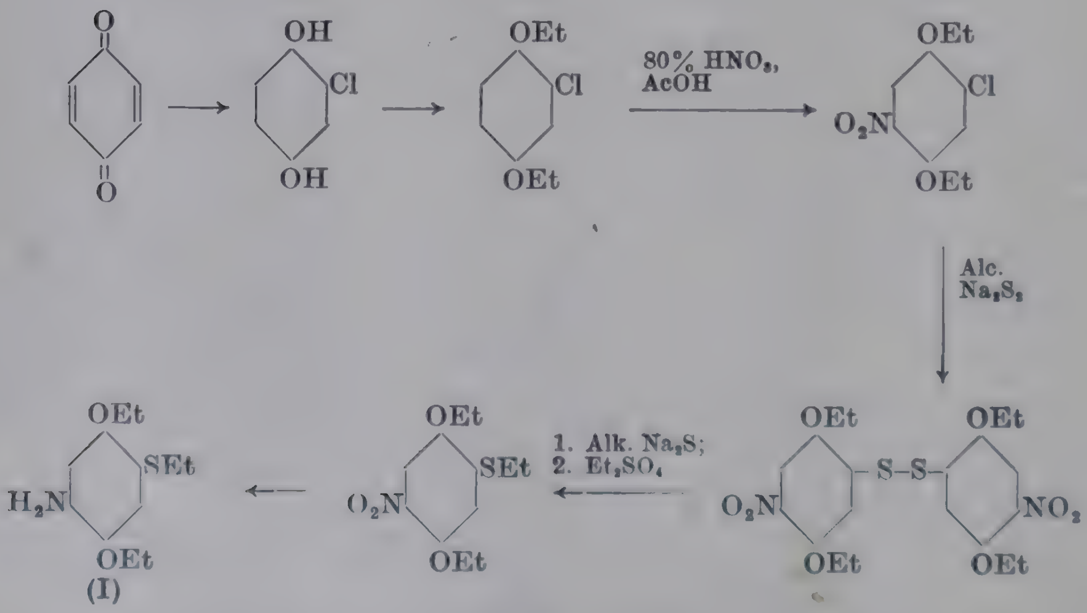
(12.90 kg.), and Acid Violet 4BL (0.275 kg.). (The small amount of acid color in this and the following formulas are used for " sighting " the coating solution, i.e., rendering it visible). (*b*) Blue BB Salt (6.79; 100%), Diazo GD (3.23; 100%), zinc chloride double salt of diazotized 4-amino-2,5,4′-triethoxydiphenyl, boric acid (24.23), aluminium sulfate (24.23), and Neptune Blue (0.14). *Developers*: (*a*) Anhydrous sodium acetate (25), borax (5), sodium bicarbonate (12.5), common salt (17.5), phloroglucinol (1), H-acid (0.36), and Prestabit oil (0.47). (*b*) Anhydrous borax (3.6), trisodium phosphate (5.6), phloroglucinol (0.8). (*c*) Anhydrous sodium acetate (22.71), sodium citrate (25.0), acid sodium tartrate (0.47), phloroglucinol (1.25), and Leonil S (0.573). (*d*) Sodium carbonate (9.31), calcined borax (6.20), sodium thiosulfate (6.20), NW-acid (2.48), resorcinol (0.62), and saponin (0.19).

The second diazo print process, in which both components of the azo dye are applied to the paper simultaneously and coupling after exposure to light is effected by exposure to ammonia vapor or other treatment not involving wetting of the paper, has superseded the first method.

The amines constituting the diazonium components in Ozalid paper were the following: (1) *p*-aminodimethylaniline; (2) 1-amino-2-naphthol-4-sulfonic acid; (3) *p*-aminodiphenylamine; (4) 4-benzamido-2,5-diethoxyaniline (Blue BB); (5) 2,5-diethoxy-4-ethylmercaptoaniline (I), prepared as in Chart 1; (6) 5-diethylaminoanthranilic acid (II), prepared as indicated;

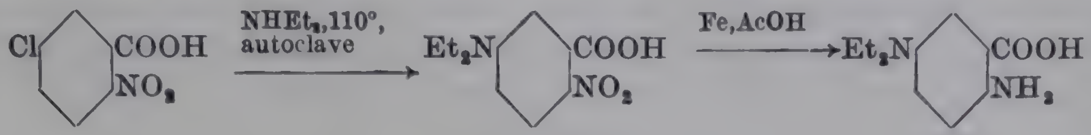
CHART 1

PREPARATION OF 2,5-DIETHOXY-4-ETHYLMERCAPTOANILINE

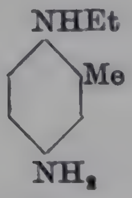


(7) 6-monoethylamino-*m*-toluidine (III), prepared by the nuclear nitrosation and reduction of monoethyl *o*-toluidine; and (8) *p*-amino-β-hydroxy-

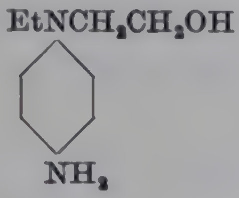
diethylaniline (IV), prepared from monoethylaniline by condensation with ethylene chlorohydrin, nitrosation, and reduction. Stabilization of the diazonium salts was effected as the diazo oxide in the case of 1-amino-2-naphthol-4-sulfonic acid, as the chlorobenzenesulfonate in the case of (II), and as the zinc chloride double salt in the other cases.


Cl
COOH
NO₂
NHEt₂,110°,
autoclave
Et₂N
COOH
NO₂
Fe,AcOH
Et₂N
COOH
NH₂

(II)

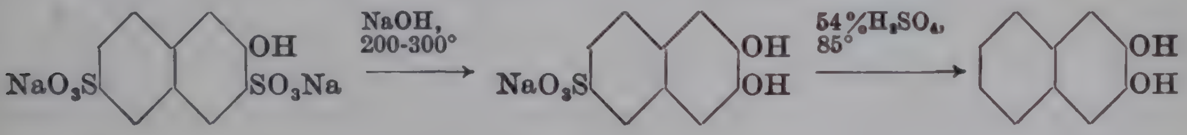


(III)


EtNCH₂CH₂OH
NH₂

(IV)

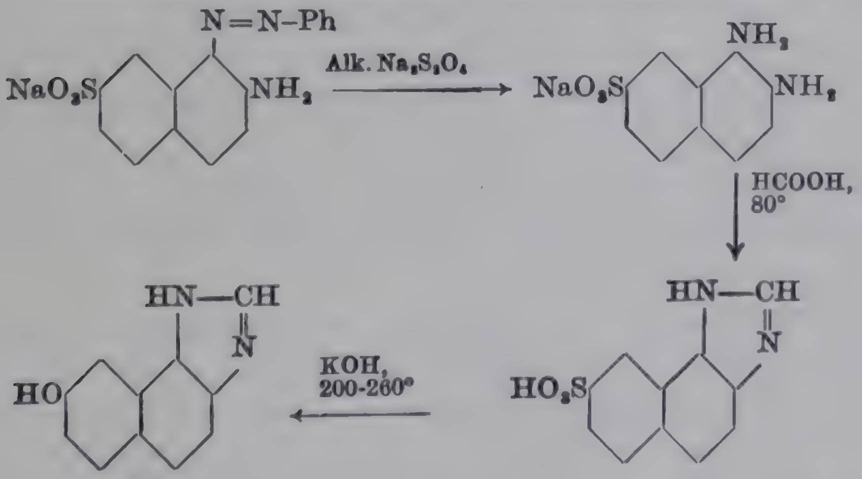
The coupling components mainly used were acetoacetanilide, resorcinol, phloroglucinol, 2,3-dihydroxynaphthalene[131] (V) (prepared from R-salt), R-salt, 1-diguanido-7-naphthol, and 8-hydroxy-(1,2)-naphthimidazole (VI) (prepared as in Chart 2). When hydroxynaphthimidazoles are used as coupling agents, the prints are fast to light and the ground does not become yellow on storage.[132]


OH
NaO₃S
SO₃Na
NaOH,
200-300°
NaO₃S
OH
OH
54%H₂SO₄,
85°
OH
OH

(V)

CHART 2

PREPARATION OF 8-HYDROXY-(1,2)-NAPHTHIMIDAZOLE


N=N-Ph
NaO₃S
NH₂
Alk. Na₂S₂O₄
NH₂
NaO₃S
NH₂
HCOOH,
80°
HN—CH
N
HO₃S
KOH,
200-260°
HN—CH
N
HO

(VI)

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[131] Cf. Kalle and Co., BP 496,090.

[132] Kalle and Co., BP 523,922.

Two typical formulas for Ozalid coating solutions are appended, the figures within parentheses representing the weight in grams for 10l. of solution: (*a*) Tartaric acid (450), zinc chloride double salt of diazotized *p*-aminodimethylaniline (424), boric acid (196), aluminium sulfate (378), resorcinol (150), thiourea (450), naphthalene-1,3,6-trisulfonic acid (400), dextrin (300), polyglycol (300), Alizarin Irisol RL (4). (*b*) Tartaric acid (150), diphenylamine-4-diazonium sulfate (139), naphthalene-1,3,6-trisulfonic acid (250), thiourea (270), Alkali Violet (6.6), R-salt (660; 80%), and polyglycol (200).

In addition to Ozalid paper, Kalle had developed cellulose film for motion picture projection prints ("Ozaphane"), acetate sheet foil for producing a continuous-tone red negative image, a polyvinyl plastic film ("Astralon"), a process (Aluna process) for making Ozalid prints from existing prints, a method for obtaining strong prints from the weak lines of pencil drawings on tracing paper, and a lithoplate process.

Some improvements suggested in the patent literature can be mentioned. Addition of a water-soluble quinone increases the light sensitivity of diazo compounds.[133] Stability of a diazotype material is increased by addition to the coating solution of a small percentage of cinnamic acid or similar acrylic acid derivative.[134] Addition to a diazo type coating composition of a film-forming substance (e.g., plasticized cellulose acetate) in an organic solvent gives a layer free from lines and curl.[135] On development with ammonia the reproduction is so good as to enable further copies to be made from the prints. Use of a polystyrene or acrylic ester resin as a binding agent and addition of an alkali and a water-absorbing substance (e.g., starch) to the diazonium and coupling components permit development by water alone.[136] Development by means of electrolytic action has been suggested, the fibrous sheet being treated with a diazotizable heterocyclic amine, an ionizable nitrite, an inorganic salt as electrolyte, a coupling component, and an alkali to prevent diazonium salt formation until the sheet is submitted to electrolysis.[137] The diazo process has been applied to produce a light-sensitive layer on a metal plate[138] and to the preparation of phototemplates.[139]

Diazosulfonates. In contrast with the decomposition of diazonium salts by light, utilized in the Ozalid type of diazo reproductions, activation of the stable *anti*-diazosulfonates to the *syn* form by means of light and the ability of the latter to couple with a phenol can be used, as mentioned in the section on diazosulfonates, for production of negative-type diazo papers. Kalle and Co. have claimed the use of diazosulfonates having two nuclear ether groups but no nuclear amino or substituted amino groups, and particularly of the diazosulfonates of 1,4,2,5-NH_2-C_6H_2YZZ in which Y and one Z are alkoxy groups and the other Z is chlorine.[140] The process, however, presents practical difficulties and has not attained commercial success.

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[133] Poser, USP 2,322,982.

[134] Reichel, USP 2,354,0[illegible].

[135] Leuch, BP 563,804; see also Hall, Harding, Ltd., and Leuch, BP 571,802.

[136] N. V. Philips Gloeilampenfabr., BP 524,786.

[137] Solomon, USP 2,419,296; 2,421,367; see also Clark, BP 587,540; Greig, USP 2,451 331.

[138] Philips Lamps, BP 534,341; Sease and Woodward, USP 2,405,523.

[139] Entwistle and Scholefield, BP 563,547.

Diazosulfonates can also be used for production of the Ozalid type of paper yielding positives from positives, the process depending on the conversion of the *anti*- to *syn*-compounds by light, followed by destruction of the *syn*-diazosulfonates by the further action of light. The undecomposed portions under the positive are then developed by heat treatment.[141] The disadvantages of the method are the considerably increased time required for the decomposition of the diazosulfonates in comparison with that of the zinc chloride double salts, and the deleterious action on the paper of the high temperature necessary for development. The use of diazosulfinates has been suggested in a recent patent.[142]

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[140] Kalle and Co., BP 518,129.

[141] Kalle and Co., USP 2,217,189.

[142] Sprung, Schmidt and General Aniline and Film, USP 2,465,760.

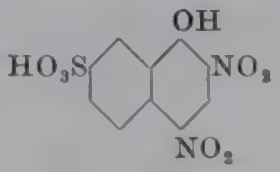
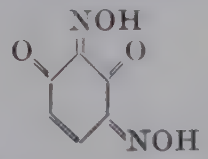
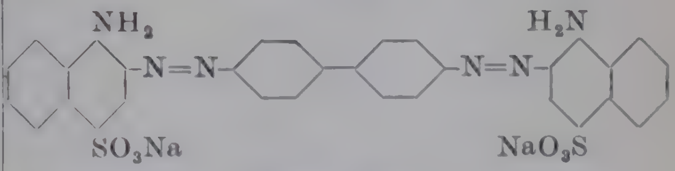
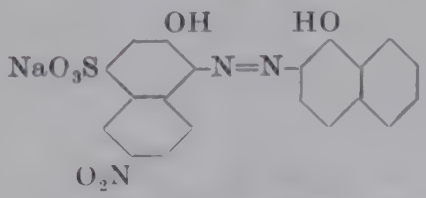
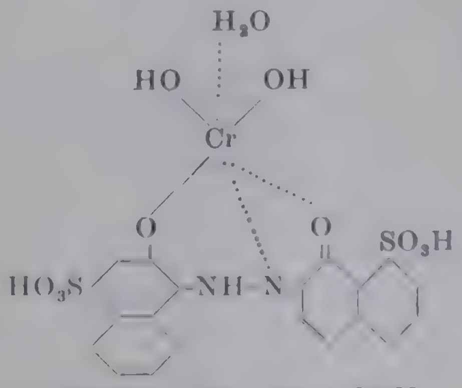
Chapter V

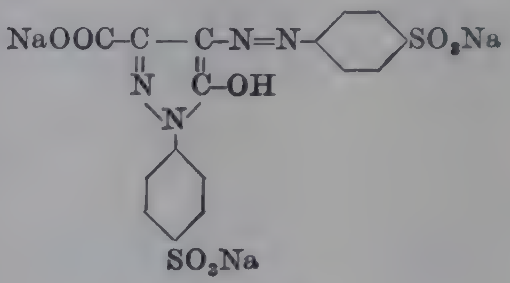
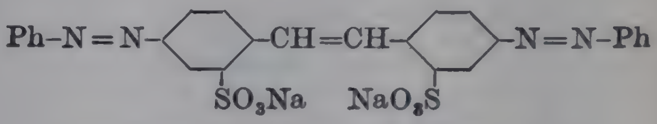
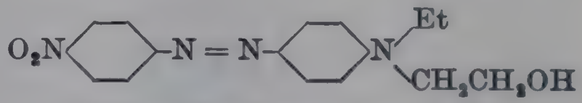
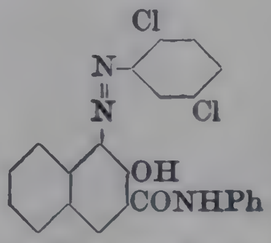
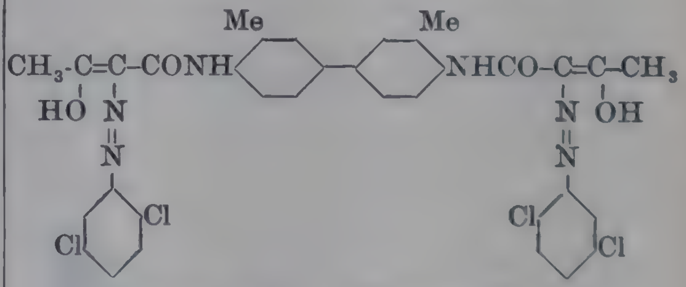
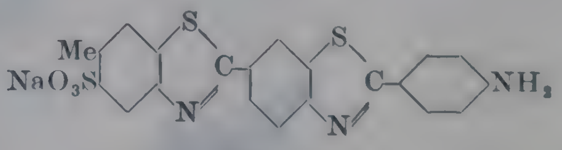
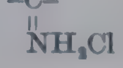
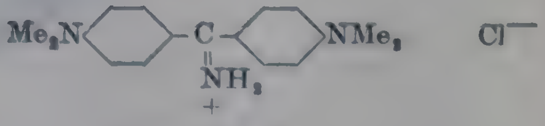
CLASSIFICATION OF DYES

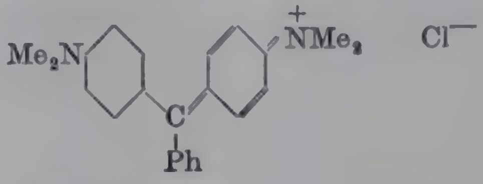
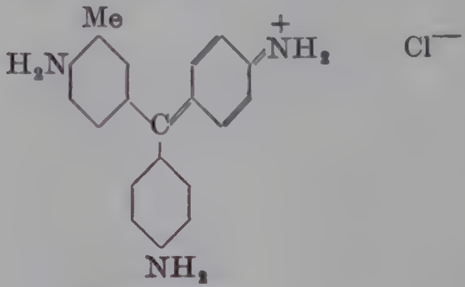
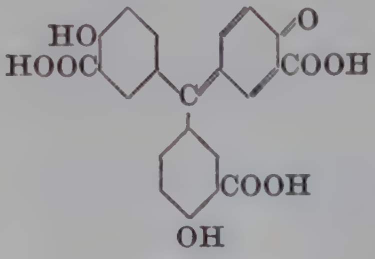
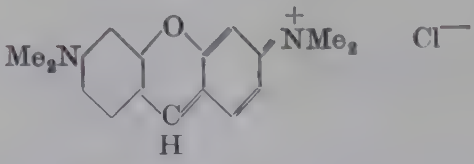
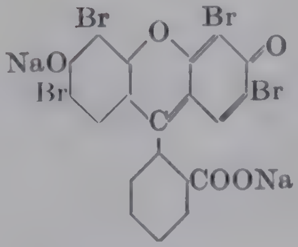
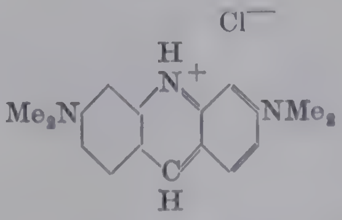
Dyes may be classified in accordance with their chemical constitution or their application to textile fibers and for other coloring purposes. To some extent there is common ground between the two methods of classification, since certain groups of dyes, such as the sulfur colors, have perforce to be dyed by methods dependent on their chemical character. Further, the dyeing properties are useful for sub-division of a large group of dyes such as the azo or anthraquinone dyes. Thus the basic classification of the anthraquinonoid dyes indicates the fundamental nucleus from which all the dyes in the series are derived, but for a detailed consideration it is convenient to divide the group into cellulose acetate, mordant, acid, and vat dyes.

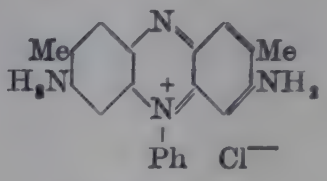
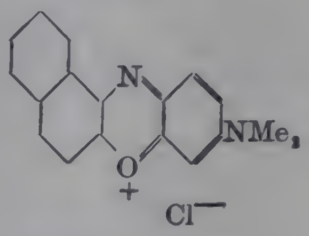
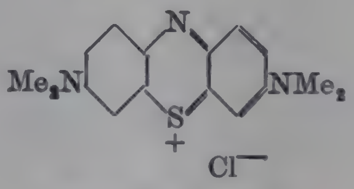
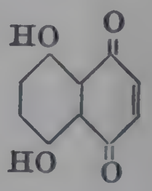
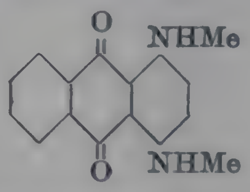
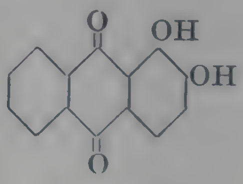
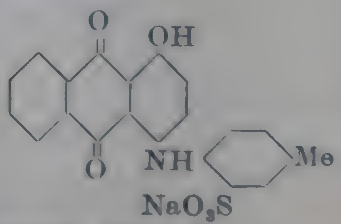
Witt suggested in 1876 a classification of dyes according to the chromophores or essential color-producing groups, but color-constitution relationships are now known to be extremely complex; and for a systematic treatment of the chemistry of dyes a classification based primarily on characteristic structural units is more satisfactory. The azo group, the anthraquinone nucleus, and heterocyclic ring systems (e.g., pyrazolone, thiazole, acridine, thiazine, oxazine) are examples of structural units which provide a simple basis of division and subdivision. Methods of preparation and application are also useful for classification. Although the nitro group occurs in numerous dyes, the class name of nitro dyes is restricted to the nitrophenols and the nitroarylamines in which the nitro group is a vital factor in the production of color and dyeing properties. Since the process of thionation or sulfurization is distinctive and the constitution of the products is largely unknown, it is an advantage to group all the dyes prepared by this general method and separate them from other sulfur-containing dyes. The thiazoles are classified separately because the thionation products are not used directly like the sulfur or sulfide dyes, but as intermediates for the preparation of azo or other dyes. The cyanine dyes and the phthalocyanines are placed in classes of their own. The cyanine dyes (with few exceptions) are used as photographic sensitizers; although they are now very large in number and are derived from a variety of heterocyclic intermediates, there are structural features common to the entire series. The phthalocyanines constitute a relatively small group, but they possess a new and distinct type of ring system among the synthetic dyes. Quinoline Yellow and other dyes that do not justify treatment in separate chemical classes on account of their limited number or indefinite constitution have been collected together as "miscellaneous dyes." The appended classification and the more detailed division of dyes in subsequent chapters are therefore based on the combined consideration of constitution, preparation, and application.

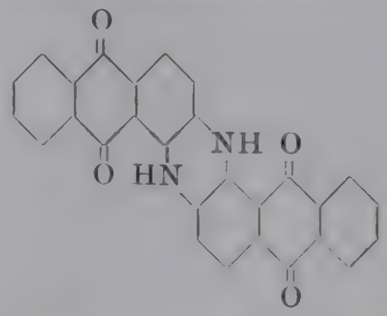
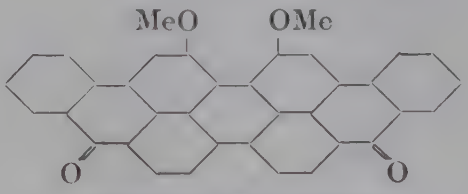
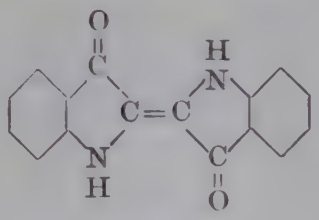
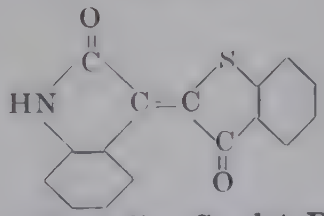
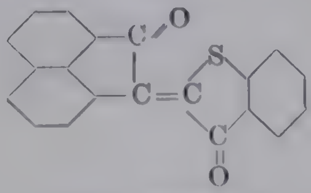
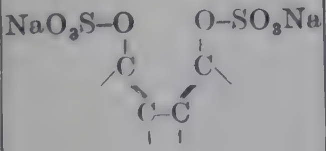
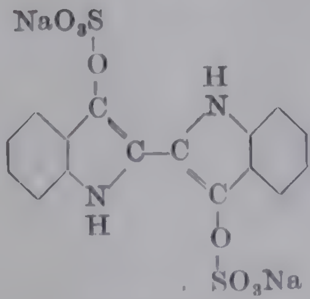
TABLE 1

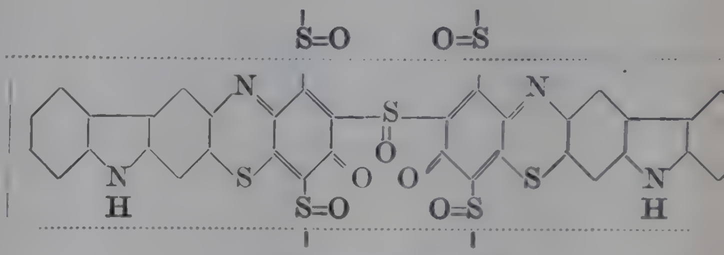
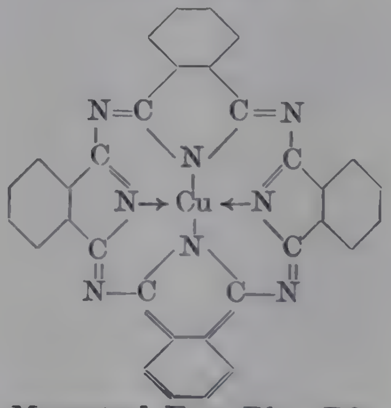
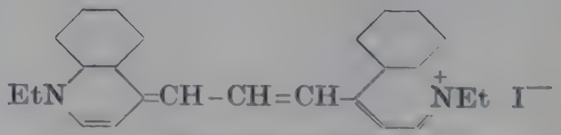
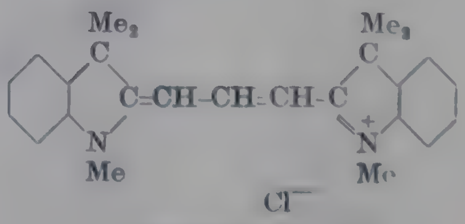
Class name of dyes	*Characteristic structural unit*	*Example*
Nitro dyes	Nitrophenol or Nitro-arylamine	 Naphthol Yellow S
Nitroso dyes	*o*-Nitrosophenol	 Fast Green O
Azo dyes (a) Soluble mono-azo or polyazo dyes	Ar–N=N–Ar′	 Congo Red
(b) Mordant dyes	*o*-Hydroxyazo group	 Eriochrome Black T
(c) Preformed metal complexes	Metal chelate	 Palatine Fast Blue GGN

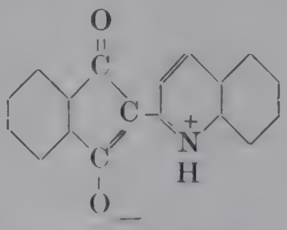
Class name of dyes	*Characteristic structural unit*	*Example*
(d) Pyrazolones	1-Phenyl-4-benzene-azo-5-pyrazolone	 Tartrazine
(e) Stilbene	Stilbene and azo or azoxy groups	 Constituent of Diphenyl Citronine G
(f) Cellulose acetate dyes	Aminoazobenzene derivative	 Celliton Discharge Scarlet B
(g) Azoic (insoluble azo dyes produced on the fiber)	(i) Derivative of β-naphthol	 Scarlet GG → Naphtol AS
	(ii) Acetoacetarylide	 Scarlet GG → Naphtol AS–G
Thiazoles	Aminothiazole- or azothiazole-sulfonic acid; or thiazolinium salt	 Primuline
Diphenylmethanes	 $-\underset{\overset{\Vert}{NH_2Cl}}{C}-$	 Auramine O

Class name of dyes	*Characteristic structural unit*	*Example*
Triphenylmethanes		
(a) Diamines (Malachite Green series)	See example	 Malachite Green
(b) Triamines (Magenta series)	See example	 Rosaniline
(c) Phenols (Rosolic acid series)	See example	 Chrome Violet
Xanthenes		
(a) Diphenylmethane derivatives	See example	 Pyronine G
(b) Triphenylmethane derivatives (Phthaleins)	See example	 Eosine
Acridines	See example	 Acridine Orange NO

Class name of dyes	*Characteristic structural unit*	*Example*
Azines	See example	 Safranine T
Oxazines	See example	 Meldola's Blue
Thiazines	See example	 Methylene Blue
Benzoquinones and naphthoquinones	See example	 Naphthazarin
Anthraquinones	Anthraquinone or anthrone	
(a) Cellulose acetate dyes	Aminoanthraquinone	 Duranol Blue B
(b) Mordant	1,2-Dihydroxyanthraquinone	 Alizarin
(c) Acid	Sulfonic acid of hydroxy- or amino-anthraquinone derivative	 Alizarin Irisol R

Class name of dyes	*Characteristic structural unit*	*Example*
(d) Vat i) Anthraquinone derivatives	Substituted anthraquinone	 Indanthrene Blue RSN
ii) Anthrone derivatives	Benzanthrone, pyrimidanthrone, etc.	 Caledon Jade Green
ndigoids (a) 2,2′-derivatives of indole and thionaphthene	$-CO-C=C-CO-$	 Indigotin
(b) 2,3′-derivatives of indole and thionaphthene		 Thioindigo Scarlet R
(c) Condensation products of indoxyl, thioindoxyl or isatin with a suitable component		 Ciba Scarlet G
lubilized vat dyes (a) Indigoids		 Indigosol O

Class name of dyes	*Characteristic structural unit*	*Example*
(b) Anthraquinonoid		
Sulfur dyes	High molecular compounds of indefinite structure, but probably containing sulfur heterocycles and disulfide or sulfoxide groups	Sulfur Black T
Sulfurized vat dyes		 Hydron Blue R
Phthalocyanines	Ring systems of four isoindole units and 4-nitrogen atoms	 Monastral Fast Blue BS
Cyanines	Heterocyclic rings united by the group $=CH(-CH=CH)_n-$, one of the rings containing quaternary nitrogen	
(a) Quinoline derivatives		 Kryptocyanine
(b) Derivatives of bases other than quinoline		 Astraphloxine FF

Class name of dyes	*Characteristic structural unit*	*Example*
scellaneous dyes		 Quinoline Yellow

Chapter VI

APPLICATION OF DYES

The organic coloring matters are used for a wide variety of purposes, but their application to textiles is so important that it is only this aspect which will be considered in some detail. Dyeing and printing, fastness tests and standards, and the treatment in general of the properties of dyes thus refer to textile fibers, unless otherwise specified; and one of the objects of this chapter is to explain the terms employed in the textile coloring industries.

The manufacture of a finished fabric from a fiber involves a long series of operations, divisible into two groups. One consists of mechanical treatments in which the masses of fibers in random order are opened out, carded, combed, spun, and woven. In the second group, of mainly chemical processes, three stages are usually distinguished: (1) preparatory or cleansing treatments—desizing, scouring, and bleaching; (2) the application of dyes; and (3) finishing treatments designed to produce luster, resistance to shrinkage and creasing, and other desirable qualities of feel and appearance. These processes need not be carried out in the stated sequence; finishing treatments frequently precede the dyeing of wool, and for cotton the dyeing process may be interposed between two preparatory treatments.

Dyes are applied to textile fibers by two distinct processes—dyeing and printing, of which the former is much more extensively used. In dyeing the fiber absorbs the dye from an aqueous solution or dispersion, and is more or less uniformly colored. The solution of the dye is the dye liquor or dyebath, and as the dyeing proceeds the concentration of the dye increases in the fiber and decreases in the bath. Ultimately under favorable conditions, there is practically no dye in the dyebath, which is then said to be exhausted. The uniformity of the dyeing (level dyeing) depends on the absorptive power of the fiber, the nature of the dye, and the conditions of dyeing. The dyed shade usually must be matched against a sample, and the fastness of the dyeing (i.e., the resistance to bleaching and other treatments or to light and other agencies) must conform to specified requirements. Many variations of the dyeing process are possible, and in particular, dyeing may be effected at any convenient stage in the series of mechanical operations by which a natural or synthetic fiber is converted into a fabric. Thus cotton may be dyed in the form of the loose fibers (raw stock), sliver, yarn (and this again in one of several forms such as hanks, cops, cheeses, beam warps, and ball warps), or fabric (piece dyeing). Wool may be dyed as loose wool, combed worsted fibers (tops or slubbing), yarn, and cloth. Both yarns and fabrics may consist of more than one kind of fiber; cotton-wool and rayon (staple fiber)-wool combinations are common, and the dyeing of such unions presents many problems. Hosiery dyeing is a separate and important branch of the dyeing industry. Furs, hats, and ribbons are other examples of fibrous materials which may be dyed. Garment dyeing has its special features and does not come within ordinary dyehouse practice.

Dyeing may be a hand operation by the simple process of moving the fibrous material, especially cotton hanks loaded on wooden sticks, in an open vat or dyebeck containing the dye liquor. This is still practised in India and China and indeed has some advantages, but machine dyeing is increasingly in use. Because of its cheapness and its ability to withstand the action of most of the reagents involved in dyeing, wood is the main material of construction for dye vats, sticks from which yarn is suspended, guide rollers, and rollers for batching cloth. Monel metal and stainless steel have the advantages of superior resistance to chemical action and of being easily cleaned and made ready for the next operation, so that in spite of the much higher cost they are now being used in the dyehouse. For handling delicate silk and rayon materials porcelain equipment is very suitable.

There are two broad types of dyeing machinery. In one, which is the mechanical analog of hand dyeing, the yarn or cloth is moved in the dyebath, which is stationary except for the agitation of the liquor due to the movement of the yarn or cloth; piece dyeing is almost invariably carried out on such machines, *e.g.*, the Lancashire jigger in which a batch of cloth is rolled off and on between a pair of wooden or ebonite rollers set above a dyebeck through which the cloth is guided in its passage to and fro. Cellulose and viscose fabrics can also be dyed by a continuous process, using a padding machine which consists of a dyebeck of relatively small volume provided with guide rollers, together with two or more squeezing rollers; impregnation is effected by passing the fabric continuously through the dye liquor and through the nip or nips between the squeezing rollers. More than one padding machine in series may be used, and they may be followed by a series of boxes in which the fabric is given the various rinsing, soaping, and other aftertreatments that may be necessary. Wool, worsted, silk, and rayon fabrics are largely dyed on a winch, a machine in which a winch or reel, provided with a mechanical drive, is set above a dyebeck. The fabric, which is passed over the reel in rope form or in open width and has its two ends sewn together, works continuously in and out of the dyebath. In the second or package type of dyeing machine, the fibrous material (raw stock, or yarn in the form of packages such as cops and cheeses) is suitably supported and the dye liquor is forced through it by means of a pump, constant circulation with periodical reversal of the direction of flow being maintained. Machines useful for special purposes are also available in which both the material and liquor are kept in motion.

The primary factor that determines the choice of one of these procedures, as well as the choice of a dyestuff, is the nature of the fiber. The chemical constitution and the physical structure of a fiber are concerned in its behavior towards dyes, and since dyeing involves the use of acids, alkalis, and oxidizing agents, their action on the fiber also must be taken into account.

TEXTILE FIBERS

Apart from the recent innovation of glass and asbestos fibers, textile fibers[1] are organic and are divisible into four chemical classes: (1) cellulose and the modified celluloses; (2) proteins; (3) synthetic polyamides, imitative of the natural proteins; and (4) miscellaneous high polymers. Another line of demarcation is between (*a*) vegetable fibers such as cotton, flax, ramie, the regenerated celluloses, and jute; and (*b*) animal fibers such as silk, wool and other animal hairs, and the fibers made from casein; the two types therefore correspond to the first and second chemical classes of cellulose and protein fibers. Textile fibers may be further divided according as they are of natural origin (such as cotton, wool, and silk), semi-synthetic (such as cellulose acetate and the casein fibers), or synthetic (such as the polyamides and the polyvinyl derivatives). It is at once apparent that the widely different chemical character of these fibers will have a profound influence on the affinity (or substantivity) of dyes and on the permanence of the fiber-dye combination—in other words on the dyeing and fastness properties of the dyes. Keeping in view the present position and the possibilities in the development of the semi-synthetic and synthetic fibers on the one hand and of dyes on the other, the tremendous complexities of the science and art of coloring textiles are also apparent. The behavior of dyes towards the various textile fibers and the methods by which the fixation of the dyes on the fibers in a more or less irreversible manner can be effected provide a basis for a classification of dyes, which is a useful supplement to the purely chemical classification (Chapter V). Among the natural fibers cotton and wool are by far the most important,[2] and since they respectively belong to the two major classes of the cellulose and protein fibers, the ability of a coloring matter to dye either of these fibers directly is in general the first consideration in assessing its dyeing properties.

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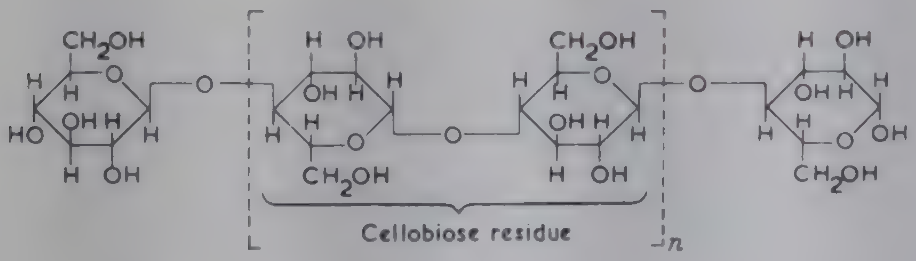
[1] Mauersberger, Matthews' Textile Fibers, 5th ed., Wiley, New York, 1947; Olney, Textile Chemistry and Dyeing, Part I, Chemical Technology of the Fibers, 9th ed., Lowell Textile Associates, Lowell, Mass., 1945; Sherman and Sherman, The New Fibers, Van Nostrand, New York, 1946; Diserens, Neueste Fortschritte und Verfahren in der chemischen Technologie der Textilfasern, 2nd ed., Birkhaüser, Basel; translated by Wengraf and Baumann, Reinhold, New York, 1948; Preston *et al.*, Fiber Science, Textile Institute, Manchester, England, 1949.

The cotton fiber is the hairy covering of the seeds of various species of the cotton plant (*Gossypium*); among the commercial varieties of cotton used for spinning, the length (or staple) of the fiber varies from about 10 mm. and the diameter from about 0.021 mm. for low quality Indian cotton to a length of 50 mm. and a diameter of 0.014 mm. for the finest Egyptian or Sea Island cotton. Under the microscope the fiber[3] is seen to be a flat twisted ribbon, consisting of a cuticle, a secondary cellulose thickening and a central canal or " lumen "; abnormal fibers, which leave undyed or lighter dyed specks in the dyed material, may have little or no secondary thickening (immature and dead cotton). When freed from natural and adventitious impurities, the cotton fiber consists of nearly pure cellulose. The natural impurities, about 10% of the weight of the fiber, are moisture (about 5%), oils and waxes, pectins, albumins and mineral matter, and a minute amount of coloring matter (gossypol). The object of scouring and bleaching cotton materials is the removal of these impurities, and when carried out under conditions in which degradation of the cellulose is avoided, it is possible to prepare a product containing over 99.8% of α-cellulose (insoluble in 17.5% aqueous caustic soda). Cellulose has the composition $(C_6H_{10}O_5)n$, n (or D.P., the degree of polymerization) being at least 1,000 for cotton cellulose; and it is a chain polymer of cellobiose residues. Cellobiose is a β-glucoside of glucose, and the linkage between each successive



Cellulose chain

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[2] The estimated world production of the four major clothing fibers in 1946–47 was as follows in thousands of metric tons; the figures within brackets are the percentages: Cotton, 4661 (72.6); Wool, 986 (15.4); Silk, 16 (0.2); Rayon, 758 (11.8) (*World Fiber Survey*, F.A.O., August, 1947).

[3] For a review of the fine structure of the cotton hair, see Hock, Ramsay, and Harris. *Text. Research* **11**, 200 (1941).

pair of cellobiose units is formed by the loss of a molecule of water. By the action of acids and oxidizing agents, as well as other agencies such as heat, light, and microorganisms, the cellulose chain undergoes degradation, and the products (hydrocelluloses and oxycelluloses) of hydrolytic and oxidative attack have progressively decreased tensile strength. Cotton subjected to mercerization, the action of strong (about 25%) caustic soda solution at a low temperature while the yarn or fabric is held under tension, has increased affinity for dyes; the object of mercerization, which is applicable only to the longer staple cottons, is to increase the luster and tensile strength. One important result of the knowledge of the constitution of cellulose has been that methods have been devised and standardized for the assay of cellulose quality. While cellulose cannot be estimated directly like simpler organic compounds which take part in reactions in stoichiometric proportions, and its purity cannot be examined in terms of readily determinable physical properties such as melting point or refractive index, it has a number of measurable characters,[4, 5] of which the two most widely used are the reducing power in terms of the copper number and the size of the chain molecule in terms of the viscosity in cuprammonium solution. Estimation of the noncellulosic constituents, such as moisture, inorganic salts, fats, waxes, and nitrogenous material, provides additional data.

The chemical properties of cellulose, notably its sensitivity to acids and oxidizing agents, have to be kept in view in submitting cotton materials to scouring, bleaching and finishing treatments. The usual scouring processes consist in treatment for several hours with 0.5–0.8% caustic soda solution (corresponding to about 3% caustic soda on the weight of the cotton) at about 130° in a pressure kier, the alkaline liquor being circulated through the material by a pump. Various additions of wetting agents and detergents may be made, and part of the caustic soda may be replaced by soda ash. For dyed materials, instead of caustic soda, soda ash or another mild alkali is used at a temperature of about 60°. Bleaching is carried out by sodium or calcium hypochlorite solution (2–3 g. chlorine per liter) at room temperature, followed by a treatment (souring) with about 0.5% hydrochloric or sulfuric acid and repeated washing with water to remove the last traces of chlorine and acid. The bleach liquor must be

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[4] Doreé, The Methods of Cellulose Chemistry, 2nd ed., Chapman and Hall, London, 1947.

[5] Marsh and Wood, The Chemistry of Cellulose, 3rd ed., Chapman and Hall, London, 1945.

kept alkaline; the maximum formation of oxycellulose takes place at pH 7. Bleaching with hydrogen peroxide or with a combination of chlorine and peroxide is being increasingly practised with the object of obtaining a better and more permanent white, simultaneously with the elimination of the degradation or tendering of cellulose. A more recent bleaching agent is sodium chlorite ($NaClO_2$). Cotton materials are also submitted to finishing treatments in order to impart in a temporary or relatively permanent manner various physical properties such as a desired feel or handle, smooth and lustrous appearance, water-repellancy and crease-resistance. The last for instance involves treatment with resin components, especially urea and formaldehyde or urea-formaldehyde condensates (Tootal process), followed by curing at high temperatures (110–130°). These processes of mercerization, scouring, bleaching, and finishing have to be considered in the choice of dyes and in assessing the range of utility of a given dye.

Vegetable fibers other than cotton consist of compound or modified celluloses, in which cellulose occurs in combination or association with lignin, pectin, and other substances. The dyeing properties, in comparison with those of cotton, are modified in accordance with the nature and proportion of the noncellulosic constituents. The flax plant (*Linum usitatissimum*), the seeds of which are valued for their oil (linseed oil) yields a bast fiber (linen), next in importance to cotton and jute among the vegetable fibers. In the natural state linen fiber is embedded in pectic substances, but when these are removed by biological or chemical processes of decomposition (retting), the residue is nearly pure cellulose, which is then similar to cotton in its dyeing properties, except for penetration difficulties due to the thickness of the cell walls of the linen fiber. Ramie (China grass) is perhaps the least lignified of the bast fibers; like flax it contains intercellular pectic materials and, when these are removed by degumming processes, a cellulose of high purity is obtained. Ramie, however, is almost valueless as a textile fiber because of its poor spinning qualities. **The jute fiber,** one of the principal economic products of India and Pakistan, is a lignocellulose or bastose in which the noncellulosic part of the molecule contains aromatic ring systems. In its chemical reactions and behavior towards dyes jute is markedly different from cotton, and somewhat similar to cotton treated (mordanted) with tannic acid. Jute thus has an affinity for basic dyes, and it has been shown[6] that this is due, not to the lignin, but to carboxyl groups in the lignin-free holocellulose fraction. Sisal (*Agave sisalana*), largely used for rope, matting, and hat manufacture, is a leaf fiber, which is also a lignocellulose; it is readily dyed both by direct cotton dyes and by acid dyes normally applied to wool, and as a result of the presence of a small amount of tannin it also takes up basic dyes.

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[6] Sarkar *et al.*, *Nature* **157,** 486 (1946); *et sequa.*

The rayons[7] produced from cellulose are of two types from the dyeing point of view. Nitro rayon (Chardonnet silk), cuprammonium (or Bemberg rayon), and viscose, which are regenerated celluloses and can therefore be dyed by the classes of dyes used for cotton, belong to one type. Cellulose acetate (acetate rayon; Celanese; Acele; Seraceta) represents the second and quite distinct type; being an ester of cellulose, it is water-repellant and has entirely different dyeing properties which depend essentially on the fiber functioning as an organic solvent. Cellulose acetate dyes are for this reason treated as a separate class.[8] Esterification can be employed for rendering cellulose resistant to dyeing by the direct cotton dyes. Immunized cotton is useful for the production of two-color effects by dyeing a fabric made up of treated and untreated yarn. In the Cotopa process (Sandoz), immunization is effected by direct partial acetylation (e.g., monoacetylation) of cellulose under conditions in which the product remains insoluble in the acetylation mixture.

Nitro rayon, historically the first (1884) and now obsolete, was produced by the evaporation of an alcohol-ether solution of cellulose nitrate, followed by denitration of the filament by means of ammonium sulfide solution. Bemberg rayon is the product of the precipitation of cellulose dissolved in an ammoniacal solution of copper hydroxide (Schweitzer's reagent), the usual coagulating agents being water, alkaline glucose, and weak sulfuric acid used in succession; a stretch spinning technique is employed by which the plastic filament emerging from a large-holed spinneret is drawn out to increased length and narrower diameter. In the viscose process alkali cellulose (I), obtained by the action of caustic soda solution of mercerizing strength on bleached sulfite pulp, is broken up and treated with carbon disulfide to yield the orange-colored gelatinous cellulose xanthate (II). The viscous colloidal solution in dilute aqueous caustic soda is aged or ripened when complex reactions take place in which the relative proportion of the carbohydrate to sulfur increases as in (III) and (IV). This liquid is then forced through spinnerets (each of which has a large number of fine orifices) into a coagulating bath of weak sulfuric acid, sodium sulfate, and glucose. The filament passes under tension over a bobbin into a Topham box, a can revolving at a speed of a few thousand r.p.m.; the centrifugal action causes the filaments to be twisted and fed on to the walls of the rotating can and a cake of viscose is thus produced. The cakes are

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[7] The term "artificial silk" is in disfavor, since the rayons are not a substitute for silk. The ASTM definition of rayon is "a generic term for filaments made from various solutions of modified cellulose by pressing the cellulose solution through an orifice and solidifying it in the form of a filament."

[8] See Chapters XXI and XXVII.

$$\left[C_6H_7O_2(OH)_2ONa\right]_n \xrightarrow{CS_2} \left[C_6H_7O_2(OH)_2O\text{–}CS\text{–}SNa\right]_n \longrightarrow$$

(I) (II)

$$\left[(C_6H_9O_4)_2(OH)\text{–}O\text{–}CS\text{–}SNa\right]_n \longrightarrow \left[(C_6H_9O_4)_3(OH)_2\text{–}O\text{–}CS\text{–}SNa\right]_n$$

(III) (IV)

removed, desulfurized by treatment with sodium sulfide solution, bleached, washed, and dried. These processes may also be carried out after reeling the cakes into skeins. Staple fiber consists of short cut-up filaments which can be mixed with cotton or wool and spun on the usual machinery for the natural fibers; staple fiber now represents over half the total production of rayon and is likely to replace filament rayon more or less completely in course of time. While the quality of cotton yarn is defined by the *count*, which is the number of hanks of 840 yards which make a pound, the quality of rayon is defined inversely by the *denier*, which is the weight in deniers (one denier $=0.05$ g.) of 450 meters. Viscose in sheet form (cellophane), largely used as wrapping material, is obtained when a wide narrow slit replaces the spinnerets.

Acetate rayon, which corresponds approximately to cellulose diacetate, is prepared by treating cellulose in glacial acetic acid with acetic anhydride and a little sulfuric acid to yield the triacetate, and partially deacetylating to the diacetate, which is precipitated by water. The white flocculent mass is dissolved in acetone, and the filaments spun by extrusion into a chamber of warm air. When the filaments are twisted and wound on to bobbins, no further treatment is necessary. Acetate rayon is more expensive than viscose, but is valued for its attractive appearance and handle, higher wet strength, and heat-insulating properties. Viscose and cuprammonium rayon are about as inflammable as cotton, but fire hazards are considerably less with the acetate. Fortisan is a rayon with dyeing properties similar to those of the regenerated celluloses, and is produced by subjecting acetate rayon to a mechanical treatment followed by saponification.

The attraction of the rayons when they were first introduced was their luster, but they are now valued for other properties. Delustering is frequently practised, and for viscose the main method is the incorporation of titanium oxide in the viscose sirup. Acetate rayon can be delustered similarly or more simply by treatment with aqueous solutions of soap or sulfonated oil at a pH of about 9 and a temperature just below the boiling point.

Viscose and cuprammonium rayon can be dyed by dyes applicable to cotton, but the precise procedures have to be substantially modified.[9, 10] Rayon must be carefully handled in dyeing without friction and strain. Decreased tensile strength in the wet state is characteristic of rayon, although this defect is a less serious problem now than in the early days of rayon manufacture.[11] Since each thread is composed of a large number of filaments, broken ends, fuzziness, and entanglement are troubles to be anticipated. Smooth surfaces and devices for tensionless treatment of yarns and fabrics are therefore necessary in the machine or hand equipment used for rayon dyeing. The nature of the manufacturing processes clearly indicates that complete uniformity in different batches of rayon cannot be expected, and although intensive research and stringent control of every factor in the various stages of production have minimized heterogeneous quality, some variation in dyeing properties, not merely from batch to batch but even in different skeins, seems to be unavoidable.[12] Normal and "greedy" yarns are encountered and these differences can be compensated for only by a choice of even-dyeing dyes.[9, 10] Direct cotton dyes have been classified according to their behavior towards light- and dark-dyeing viscose, and methods have also been devised for correcting variable affinity; but uniform dyeings on viscose are still relatively difficult to obtain with vat dyes,[13] which have a tendency to emphasize rather than cover up the defects in the yarn. Like cotton, viscose can be dyed in different forms—skeins, cakes, or fabrics—and each has its own problems and advantages. While cake dyeing is increasingly practised,[14] a more recent and important development is the coloration of viscose before spinning. The process of mass pigmentation or "spun dyeing" merely consists in the addition of an aqueous dispersion of a pigment (e.g., carbon black or a phthalocyanine) to the viscose sirup. The advantages of spun-dyed rayons are the much greater uniformity of the shades and the greatly improved fastness to wet treatments. Resin finishes, which are used more on rayons than on the natural fibers, are easier to carry out on the mass-pigmented rayon because of its fastness to wet processing. Many of the

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[9] See Chapters XI and XXX.

[10] Whittaker and Wilcock, Dyeing with Coal-tar Dyestuffs, 5th ed., Baillière, Tindall, and Cox, London, 1949.

[11] Special "high tenacity rayon" (Tenasco; Durafil) is manufactured for tire and parachute cords; such rayon is difficult to dye owing to the poor affinity and is little used for textiles. See also Rose, *J. Soc. Dyers Colourists* **61,** 113 (1945).

[12] Boulton and Wardle, *J. Soc. Dyers Colourists* **63,** 8 (1947).

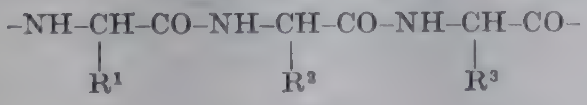
[13] Wilcock, *J. Soc. Dyers Colourists* **63,** 136 (1947).

[14] Woodruff, *Am. Dyestuff Reptr.* **36,** 549 (1947).

problems of the rayon dyer and finisher are automatically eliminated by incorporating the color in the spinning bath, and the only limitation of the process is the difficulty of using it for small quantities.[15]

Wool refers to sheep's wool, but includes the wool of certain goats (e.g., cashmere, angora, alpaca). Wool fleeces are graded and each fleece is then sorted, so that an ultimate classification is made, based on staple, fineness and other qualities. The length of the wool fiber ranges from about 2.5 to 40 cm., and the diameter from about 0.01 to 0.07 mm.; usually the shorter fibers are finer, and the longer fibers are coarser. The fiber is accompanied by suint (potassium salts of organic acids) and grease (wool fat, lanolin), which are removed by scouring with warm soap and sodium carbonate solution. The wool fiber[16] is seen under the microscope to be rod-like with surface scales pointing in the same direction, somewhat like fish scales. The surface serrations play a part in the felting[17] of wool as well as the absorption of dyes. Beneath the horny epidermis is a layer of long spindle-shaped cortical cells, the main part of the finer quality of wool fiber. The innermost medullary layer of the large round cells is more prominent in the coarser wools, being absent in some of the finest wools; and in kemps (coarse fibers of diameter 0.07 to 0.2 mm.—the counterpart of dead cotton) the medulla is developed to the complete exclusion of the cortical layer. Kemps appear as lighter dyed or undyed specks in admixture with the normal fibers, although both types absorb about the same amount of dye, the reason being that the medullated fibers refract and scatter more light.

Wool and silk are similar in dyeing properties, since both consist of proteins, but there are differences due to the nature of the side chains R in the protein molecules (V) and to the physical properties of the two fibers.



$$-\underset{\displaystyle R^1}{\underset{|}{NH-CH}}-CO-\underset{\displaystyle R^2}{\underset{|}{NH-CH}}-CO-\underset{\displaystyle R^3}{\underset{|}{NH-CH}}-CO-$$

(V)

A characteristic physical property of wet wool is its elastic extensibility to twice its length in the unstretched state; the polypeptide chains are in a folded condition (α-keratin) in the unstretched fiber and in a fully extended state (β-keratin), approximating to that of natural silk, in the stretched fiber.[17a] By treatment with steam while under tension the wool fiber can be given a " permanent set " in the stretched condition, and this property is utilized in certain finishing operations. Imparting a permanent wave to hair is similar in principle.

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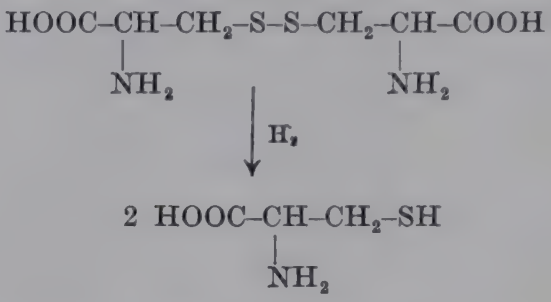
[15] See also Thomas, *J. Soc. Dyers Colourists* **62**, 309 (1946).

[16] Hock, Ramsay and Harris, *Text. Research* **11**, 415 (1941).

[17] See Freney, in Fibrous Proteins, Society of Dyers and Colourists, 1946.

[17a] Ambrose *et al.*, *Nature* **163**, 483, 859 (1949); Mizushima *et al.*, *ibid.* **164**, 918 (1949).

Wool fiber consists of one or more sulfur-containing proteins belonging to the large group of keratins. The sulfur content varies between 2.5 and 4.5%. The sulfur is present in the form of cystine, and the disulfide group is one of the links holding chains of the keratin molecules parallel.



$$\mathrm{HOOC{-}\underset{NH_2}{\underset{|}{CH}}{-}CH_2{-}S{-}S{-}CH_2{-}\underset{NH_2}{\underset{|}{CH}}{-}COOH} \qquad \text{Cystine}$$

$$\Big\downarrow \mathrm{H_2}$$

$$2\ \mathrm{HOOC{-}\underset{NH_2}{\underset{|}{CH}}{-}CH_2{-}SH} \qquad \text{Cysteine}$$

Wool is damaged by sodium sulfide solution, and therefore cannot be dyed with sulfur dyes by the normal process. The combined cystine of wool appears to be divisible into four sub-fractions which differ in their reactivity towards sodium bisulfite, alkali, formaldehyde, and thiolacetic acid.[18] Wool is stable to dilute acids, but is broken down by boiling 20% hydrochloric acid, by cold concentrated mineral acids, and by hot alkaline solutions. With increasing pH, the disulfide link suffers hydrolytic fission:

$$\mathrm{W{-}CH_2{-}S{-}S{-}CH_2{-}W} \xrightarrow{\mathrm{H_2O}} \mathrm{W{-}CH_2{-}SH} + \mathrm{W{-}CH_2{-}S{-}OH} \longrightarrow \mathrm{W{-}CHO} + \mathrm{H_2S}.$$

The stability of wool to 70% (w/w) sulfuric acid at 38° for 15 minutes and the instability to boiling 5% caustic soda solution provide alternative methods for estimating wool mixed with cellulosic fibers, which exhibit the reverse properties. Likewise, it follows that dyeing processes involving the use of hot alkaline liquors are inapplicable to wool, and in general a sharp distinction can be made between the dyeing properties of wool and those of cotton. At least 17 amino acids, besides cystine, have been isolated from the products of hydrolysis of wool, and among these are diamines (such as lysine) and dicarboxylic acids (such as aspartic acid). Thus keratin molecules are held together by salt linkages, in addition to the covalent disulfide linkages; and the amphoteric character of wool fiber permits use of dyes containing either acid groups or basic groups. In practice the great majority of wool dyeing is carried out by means of acid dyes, and the behavior of wool towards these dyes is governed largely by the number and character of the basic groups. The basic side chains of wool combine with chromic acid, and since very stable fiber-chromium-dye complexes can be thus produced by the use of dyes containing suitable groups, the application of such acid-mordant dyes to wool in conjunction with chromates and dichromates has become well established. The free amino groups in wool can be diazotized and coupled with naphthols and naphthylamines for production of yellow to brown shades.[19]

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[18] Phillips in ref. 17.

It is usually not necessary to bleach wool, since the natural cream or yellow tint is covered by dyeing, but for white materials bleaching is effected by exposure to sulfur dioxide (stoving) or by means of hydrogen peroxide in presence of sodium silicate at about 50°. The bleaching effect of sulfur dioxide is reversible, but a good permanent white is obtained by following up with a hydrogen peroxide bleach. Wool is submitted to various physical and chemical treatments in order to improve the handle and appearance and to increase the density and durability by felting. These have to be borne in mind in dyeing, so that the dyed shades employed may have the necessary fastness. In the milling (or fulling) process fabrics are submitted to pressure in the wet state in presence of soap, alkali, or acid. Crabbing is a boiling water or steaming treatment given to worsted and worsted-cotton union fabrics, at full width and under tension, in order to prevent curling and shrinking. In decatizing, steam is blown through a perforated cylinder on which the fabric is batched, the effect being to set the fiber and also impart luster. Potting (or wet decatizing) is a treatment, while the fabric is under tension in a special machine, with boiling water and steam under specified conditions, the water being neutral or faintly alkaline, but never acid; the time of treatment may extend for several hours. If the fabric contains both dyed and undyed yarn, there should be no bleeding from the colored to the white material. Fastness of dyes to potting is therefore a very stringent requirement. Loose wool and woollen cloth containing vegetable fibers are carbonized for removing the cellulose as powdery hydrocellulose; heating with 5–6% sulfuric acid at 110° is the usual method, but gaseous hydrogen chloride and aluminium chloride solution have also been employed. Chlorinated wool is produced commercially on a large scale by treatment of wool with chlorine as the gas or in aqueous solution; the objects are to improve luster and transparency, impart the scroopy feel of silk, and reduce the tendency to felt which results in shrinkage.[20] The last, the production of unshrinkable wool, is the main objective. In the Dri-Sol process a solution of sulfuryl chloride in white spirit is employed.[21] The surface structure is modified, and in consequence the affinity for dyes is increased; at the same time the fastness of the dyed shades is in many cases diminished. The dyeing of chlorinated wool therefore calls for a careful choice of dyes and the adjustment of dyeing conditions.[22] In mixed fabrics of chlorinated and unchlorinated wool two-color effects can be obtained by dyeing from the same bath. Resistance to shrinkage, like the crease-resistance of cotton fabrics, can also be achieved by resin treatment, e.g., with melamine condensates and heat curing.[23]

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[19] Mikhailenko, *Chem. Abstracts* **42,** 5676 (1948).

[20] Meunier and Latreille, *Chimie & industrie* **10,** 636 (1923); Wool Industries Research Association, BP 275,742; 417,719; Harris *et al.*, *Ind. Eng. Chem.* **40,** 2280 (1948); and numerous other papers and patents.

[21] Hall *et al.*, BP 464,503.

Silk[24, 25] is produced by the silk worm as a continuous thread in the form of a double strand of the protein fibroin, covered and cemented by a second protein, sericin (silk gum). They issue from two pairs of glands as viscous fluids which coagulate on contact with air; the long continuous filament with which the pupa thus surrounds itself is broken when the moth emerges. The pupa is killed by dry heat (about 80°) or live steam or chloropicrin in order to collect the silk from the cocoon. The silk from the cocoons is then graded and reeled into skeins; tangled and loose ends are combed and spun into the inferior quality known as spun silk. By imparting the necessary twist to single or multiple strands of the reeled silk (throwing), yarns for voile, crepe, and other special silks are prepared. Degumming of silk, the removal of sericin from the fiber, is effected by treatment with hot soap (or soap and sodium carbonate) solution; degumming is essential for bringing out the true luster of silk and as a preparation for dyeing since unlevel shades are otherwise produced. The boiled-off liquor containing an alkaline solution of sericin and its hydrolytic products is a useful addition to the dyebath which assists level dyeing. The properties of luster and scroop for which silk is prized are well known. Silk is electrified by friction and to avoid difficulties that may arise therefore in the course of manufacture, the fiber can be softened with glycerine or soap solution and by humidifying the air. After degumming, the silk fiber appears under the microscope to be a transparent, structureless rod. Careful mechanical handling is necessary to avoid damage to the fiber, resulting in diminished luster and uneven dyeing properties, but unlike rayon, silk has remarkably high tensile strength, both in the dry and wet state. Silk has high absorptive power, utilized for weighting it, usually by alternate soaking in stannic chloride and sodium phosphate solutions. While weighting is of some advantage in giving flimsy silks a full and rich feel and appearance, it tends to be used for fraudulent purposes. Like other high molecular proteins, silk fibroin is attacked by and dissolves in strong acids, hot alkalis, and ammoniacal copper oxide. The fluidity of the solution in cupri-ethylenediamine can be used for detecting and estimating chemical damage in silk.[26, 27] However, silk withstands the action of acids and alkalis to a markedly greater extent than wool. Cotton-silk union fabrics can be mercerized, if the temperature is maintained below 15°. Dilute mineral acids cause no damage, and in fact increase the luster and scroop. With increasing strength of acid the fiber contracts, and crepes are produced in this manner.

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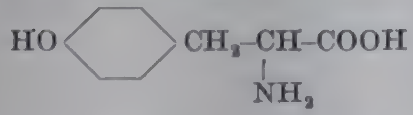
[22] Smith and Harris, *J. Research Natl. Bur. Standards* **19,** 81 (1937); Barritt and Elsworth, *J. Soc. Dyers Colourists* **64,** 19 (1948); Luttringhaus, *Am. Dyestuff Reptr.* **37,** 464 (1948).

[23] Johnstone, Van Loo, and American Cyanamid, USP 2,329,622.

[24] Cultivated or mulberry silk is regarded as true silk, distinguished from wild silk produced by certain moths other than the silk worm (*Bombyx mori*).

[25] Howitt, Bibliography of Silk, 1947.

The essential differences between the proteins of silk and wool, which adequately account for the differences in properties, are that sulfur is absent in fibroin and the side chains in the fibroin molecule are much less varied and complex than those in keratin. The polypeptide chains in silk are in the fully extended condition in contrast with the folded chains of α-keratin. From the extrapolated viscosity of fibroin in lithium thiocyanate solution, the molecular weight of fibroin is found to be 10,000–20,000, comparable with that of synthetic polyamides, but much smaller than that of keratin.[28] The main amino acids constituting fibroin are glycine, alanine, tyrosine, and serine, present in proportions[29] of about 43.8, 26.4, 13.2 and 13.6%. X-Ray examination has shown that silk has a crystalline as well as an amorphous phase. The crystallites are composed of polypeptide chains in which glycine and alanine residues alternate, and the latter is occasionally replaced by serine residues, this being possible on account of their similar size. Tyrosine is present only in the amorphous phase, as shown by the observation that when silk is coupled with diazonium salts the X-ray spectrum is unaffected.[30] In view of its character as a protein, combined with its excellent absorptive capacity, a wider range of dyes can be used on silk than on any other fiber. Even the natural coloring matters, almost completely abandoned for cotton and wool, continue to be used for silk dyeing, and nearly every type of dyestuff applicable to cotton and wool can be successfully dyed on silk. Except

NH_2CH_2COOH	Glycine
$CH_3CH(NH_2)COOH$	Alanine
$HOCH_2CH(NH_2)COOH$	Serine
	Tyrosine

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[26] Takamatsu, *J. Soc. Chem. Ind. Japan*, **36,** 566 (1933).
[27] Coleman and Howitt in ref. 17.
[28] Signer and Straessle, *Helv. Chim. Acta* **30,** 155 (1947).
[29] Coleman and Howitt (in ref. 17) have determined the percentage of tyrosine and serine as 10.6 and 12.6.
[30] Meyer *et al.*, *Helv. Chim. Acta* **23,** 1441 (1940); see also Friedrich-Freksa, Kratky and Sekora, *Naturwissenschaften*, **32,** 78 (1944).

for the precautions necessary for preserving the attractive feel and appearance of the expensive fiber, silk presents fewer practical problems in dyeing than the other fibers. Although acid and basic dyes in general are applicable to silk, neutral dyeing acid dyes and direct cotton dyes are preferred at the present time. Acid dyes may be applied in presence of boiled-off liquor, and direct dyes with the addition of Glauber's salt or soap and acetic acid. Vat dyes can be used under controlled conditions, and the relevant problems have now been largely solved.

The dyeing properties of both silk and wool, and the luster, handle, tensile strength, and dielectric properties of silk, and the high wet strength, felting properties, crimp, crease-resistance, absorptive capacity for moisture and perspiration, and warmth of wool, have led to important developments in the modification of the cellulosic fibers and in the production of semisynthetic and completely synthetic fibers having one or more of the qualities of silk and wool.

With the object of imparting to cellulose the dyeing and other properties of wool, cotton and cellulose rayons, particularly viscose, may be treated with nitrogenous materials.[31] Cisalfa, Fibramine, and Lacisana are viscose rayons containing 3–5% of casein, the protein being dispersed in the viscose sirup prior to spinning. Abrasives may be added to the coagulating bath to give a roughened surface. Artilana and Rayolanda are examples of urea-formaldehyde resin-modified viscose fibers. Methods for the " animalization " of cellulose fibers by the attachment of basic radicals to the hydroxyl groups are described in numerous patents. The simplest procedure appears to be to heat with monoethanolamine acid sulfate ($NH_2CH_2CH_2$-OSO_3H) in presence of caustic soda, when 0.56% of nitrogen can be introduced, and the product can be dyed readily by acid wool dyes.[32] Cotton may be mordanted [33] for dyeing with acid wool dyes or with Indigosols by treatment with quaternary ammonium salts such as $C_{18}H_{37}$-NMe-CO-CH_2NMe_3Cl. Cotton treated with octadecyloxymethylpyridinium chloride acquires affinity for acetate rayon dyes.[34] These methods have not met with technical success, except in finishing processes, such as treatment with formaldehyde and urea, melamine, cyanamide, or guanidine, in which the main object is to produce crease-resistance and the modification of dye affinity is incidental.

Alginic acid of seaweed in the form of its calcium and other salts has been used for fiber manufacture.[35] Calcium alginate is soluble in aqueous alkali, and the fibers therefore have very limited use; chromium and beryllium alginate fibers have greater wet strength and alkali resistance, but they have poor elasticity. Calcium alginate can be dyed with basic colors, and chromium alginate with mordant dyes.

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[31] For a review, see Wakelin, *Can. Textile J.*, **56**, No. 16, 33 (1939).

[32] Guthrie, *Textile Research J.*, **17**, 625 (1947).

[33] IG, BP 466,099.

[34] Womble, Feldmann and Dan River Mills, USP 2,430,153.

[35] Speakman *et al.*, *J. Soc. Dyers Colourists* **60**, 264 (1944); **61**, 13 (1945).

By dissolution in aqueous alkali or urea, extrusion into an acid coagulating bath and hardening by formaldehyde treatment (or other methods analogous to leather tanning), nonfibrous proteins have been converted into fibers (" Azlons " or " Prolons ") which have the thermal and some of the other properties of wool, but lack the wet strength, lofty handle and felting properties of wool As in the case of rayon, their utility is greatly increased by admixture with the natural fibers. Lanital, Lactofil, Aralac, Fibrolane, and Tiolan are casein fibers; Marena is from waste hide proteins; Ardil is from groundnut protein;[36] soybean protein has been used in Japan and the United States.[37] The artificial fibers from casein and other proteins are broadly similar to wool in dyeing properties, but there are marked differences due to the character of the different proteins and the physical structure of the fibers.[38, 39]

The discovery of **nylon**[40] is a landmark in the fiber industries, being the first truly synthetic fiber and possessing such outstandingly valuable properties that it became an established success immediately after its introduction (du Pont, 1938). In 1940 the production was 8 million pounds, and by 1945 the figure had been trebled. The brilliant work of Carothers on polymerization, commenced in 1930, culminated in the dual achievements of nylon and of the synthetic rubber neoprene. Nylon[41] is a generic name for superpolyamides prepared by the condensation of aliphatic diamines and dicarboxylic acids.[42] While innumerable superpolyamides can be made by this general method, the commercial type is made from adipic acid and hexamethylenediamine. Adipic acid is prepared from phenol via cyclohexanol[43] and cyclohexanone; and hexamethylenediamine is prepared from adipic acid via the amide and the nitrile.[44] Adipic acid can also be prepared by the oxidation of cyclohexene, a by-product in petroleum refining and by the action of carbon monoxide on tetrahydrofuran at 270°/200 atm. in presence of nickel iodide as a catalyst and nickel carbonyl as a carbon monoxide carrier.[45] The first step in nylon production is the formation of "nylon salt," m.p. 183°, probably the additive compound (VI).[46] The nylon salt may be crystallized to remove undesirable impurities.

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[36] See Thomson in ref. 17; Lundgren and O'Connell, *Ind. Eng. Chem.* **36,** 370 (1944); Traill, *J. Soc. Dyers Colourists* **61,** 150 (1945).

[37] Boyer, *Ind. Eng. Chem.* **32,** 1549 (1940); *Rayon Textile Monthly*, **25,** No. 1, 85 (1944).

[38] For a discussion of the dyeing of casein fiber, see Tattersfield in ref. 17.

[39] For a discussion of the mechanical properties of the synthetic fibers in terms of wool and silk protein fiber models, see Harris and Brown in ref. 17.

[40] Boulton, *Ind. Eng. Chem.* **34,** 53 (1942).

[41] Sigel, Nylon—a literature survey, Textile Research Institute, New York.

[42] For the first synthesis of molecules similar to fibrous proteins, see Woodward and Schramm, *JACS* **69,** 1551 (1947).

[43] *BIOS* **743.**

[44] *BIOS* **368.**

$$\mathrm{HOOC(CH_2)_4COOH + H_2N(CH_2)_6NH_2} \longrightarrow$$

$$\mathrm{\bar{O}OC(CH_2)_4CO\bar{O}\ \ H_3\overset{+}{N}(CH_2)_6\overset{+}{N}H_3} \qquad \mathrm{(VI)} \longrightarrow$$

$$\mathrm{HOOC(CH_2)_4}\left[\mathrm{-CONH(CH_2)_6NHCO(CH_2)_4}\right]_n\mathrm{-CONH(CH_2)_6NH_2}$$

Nylon

After concentration below 160°, polymerization is effected by heating in an autoclave below 270°. The reaction is stopped when a molecular weight of 10,000–20,000 has been reached. The polymer is extruded from the autoclave, by means of oxygen-free nitrogen at high pressure, into a spray of water; a ribbon 0.3 mm. thick is thus obtained, which is then cut into about 0.6 mm. square chips. The chips are dried in a rotary tumbler below 110° to prevent oxidation, and then melted in a special apparatus designed to avoid degradation of the polymeride and formation of gas bubbles. After filtering the melt through a sand filter and extrusion through spinnerets, uniform threads are obtained by passing the filaments through a cooling chimney, followed by treatment with steam, which makes the nylon less susceptible to extension with increase in relative humidity. Cold drawing, during which wetting with water reduces breakages, changes the internal structure and greatly increases the elasticity and strength of the filaments which can thus undergo an extension of several hundred per cent.

Nylon is of two types: silk-like, strong, and lustrous; or wool-like. The latter is produced by carding, baling, and steaming at 25 lbs. pressure for a few minutes to produce a permanent crimp. Molten nylon may be incorporated with a pigment dispersion in a polyester or a polyester amide.[47] Mechanical and chemical methods can be employed to produce a scaly surface structure. Nylon is used for a variety of purposes, and in particular for hosiery and other knitted goods and for the bristles of brushes. As a textile it has attractive appearance, high elasticity and wet strength, small moisture absorption, stability to acid and alkali treatments under moderate conditions, resistance to attack by microorganisms and insects, and noninflammability.

Nylon has presented some serious dyeing problems, which are gradually being solved. The affinity for acid dyes is primarily due to the terminal amino groups, although at pH below 3 combination can also occur at the weakly basic amido groups.[48] As in the case of viscose, the main difficulty in dyeing nylon is due to the high stretch (over 300%) during manufacture. Complete uniformity in the quality of the yarn is therefore difficult to attain, and the dye manufacturer and dyer have to face the problems of producing dyes and adopting dyeing processes which will tend to cover up the yarn variations. Cellulose acetate dyes, applied by the same methods, are suitable for this purpose, but unfortunately their fastness on nylon does not meet the highest requirements. Vat dyes with outstanding fastness to light when dyed on cotton exhibit inferior fastness to light on nylon.[49]

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[45] *BIOS* **351**.

[46] Coffman *et al.*, *J. Polymer Sci.* **2**, 306 (1947).

[47] Cockbain *et al.*, BP 569,170.

Perlon L is a polymer of ω-caprolactam, recently developed in Germany by the IG, who also synthesized a series of dyes specially for application to this fiber.

Vinyon[50] is a copolymer of vinyl chloride (about 90%) and vinyl acetate. It is spun from an acetone solution like cellulose acetate, and has a molecular weight of about 20,000. Its low softening point (65°) is a disadvantage, but it has uses in electrical insulation, and great stability to acid and alkali has made it a useful material for filter cloths. Vinyons of a molecular weight of the order of 8,000 can be used as a cementing material for reinforcing cotton, wool, silk, and rayon textiles. Vinyon is difficult to dye on account of its water repellancy, but in presence of *o*-hydroxydiphenyl and other assistants[51] selected acetate rayon dyes can be applied. Certain azo dyes are stated to have affinity for Vinyon.[52] Vinyon N, a copolymer of vinyl chloride and acrylonitrile, has improved dyeing properties.

Saran is a copolymer of vinylidene chloride and vinyl chloride;[53] the commercial product used for textile purposes (mainly upholstery fabrics) has a molecular weight of about 20,000 and a softening point of about 130°. The mass pigmentation method is best suited for coloring Saran.

Polyethylene (Polythene), of great value as a plastic, is being developed for textile purposes in view of its tensile strength, elasticity, and water repellancy.[54] Polystyrene (Polyfiber), drawn out from a molten mass of the material,[55] is remarkable for its extremely fine diameter (0.02 to 4 microns).

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[48] Peters, *J. Soc. Dyers Colourists* **61,** 95 (1945); Carlene, Fern and Vickerstaff, *ibid.*, **63,** 388 (1947); Boulton, *ibid.*, **62,** 65, 77 (1946); McGrew and Schneider, *JACS* **72,** 2547 (1950).

[49] See also Neunier and Saville, *Rayon Textile Monthly* **28,** 273, 379 (1947); Saville, *Am. Dyestuff Reptr.* **35,** 51 (1946); Koestler, *ibid.*, **36,** 189, 223 (1947).

[50] Bonnet, *Ind. Eng. Chem.* **32,** 1564 (1940).

[51] American Viscose Corp., USP 2,306,880.

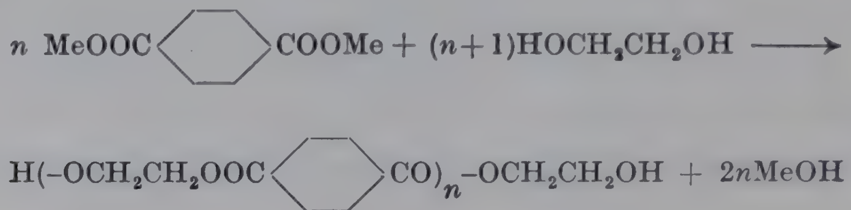
[52] Klein, Adams, and American Cyanamid, BP 568,037.

[53] Goggin and Lowry, *Ind. Eng. Chem.* **34,** 327 (1942).

[54] Hahn, Macht and Fletcher, *ibid.* **37,** 526 (1945).

[55] Dow Chemical Co., USP 2,385,358.

Terylene is a fiber-forming polymer prepared by the condensation polymerization of dimethyl terephthalate and ethylene glycol.[56] Highly oriented fibers are obtained by extrusion from the melt and cold drawing.[57]



Terylene has remarkable stability to light and hydrolysis, but the cold-drawn fibers are very difficult to dye.

Glass fibers[58] (Fiberglas) have the advantages of noninflammability and resistance to chemical and fungal attack, and are therefore useful for filtercloths, curtains, and other decorative materials; but glass fibers for clothing are only a novelty at present. Mineral pigments can be incorporated in the glass before it is drawn, and processes are also being developed for dyeing and printing glass fabrics with organic pigments dispersed in water-in-oil emulsions.[59]

IDENTIFICATION OF TEXTILE FIBERS[60]

Four types of tests are usually employed for identifying textile fibers. Mixtures of fibers are used to an increasing extent in the construction of fabrics, and all the four groups of tests have to be carried out for ensuring complete identification, especially where the newer synthetic fibers are concerned. The four tests are (1) burning; (2) microscopic examination; (3) color reactions; (4) solubilities. The burning test, carefully observed for combustibility, melting, bead formation, odor, and constituents of the ash, gives valuable information which is sometimes adequate for quick identification. The microphotographs of the longitudinal and cross-sectional appearance of the more important fibers in Chart 1 indicate the utility of microscopic examination in distinguishing one fiber from another.

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[56] Whinfield, *Nature* **158**, 930 (1946); Whinfield and Dickson, BP 578,079; Dickson, BP 579,462; Hardy, *J. Soc. Chem. Ind.* **67**, 426 (1948).

[57] Astbury and Brown, *Nature* **158**, 871 (1946); Hardy and Wood, *ibid.* **159**, 673 (1947).

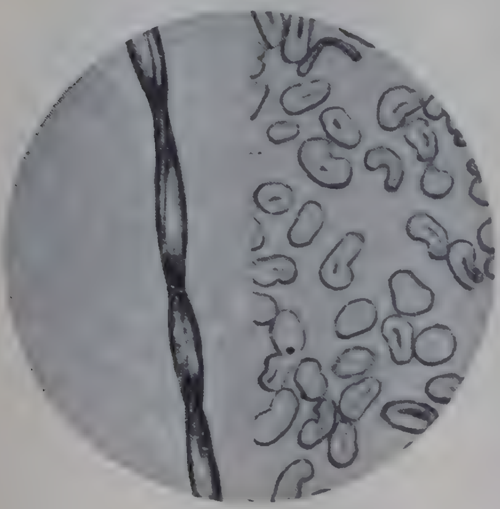
[58] Fiberglas Bibliography, Owens-Corning Fiberglas Corp., 1945.

[59] Page, *Rayon Textile Monthly* **25**, No. 11, 81 (1944).

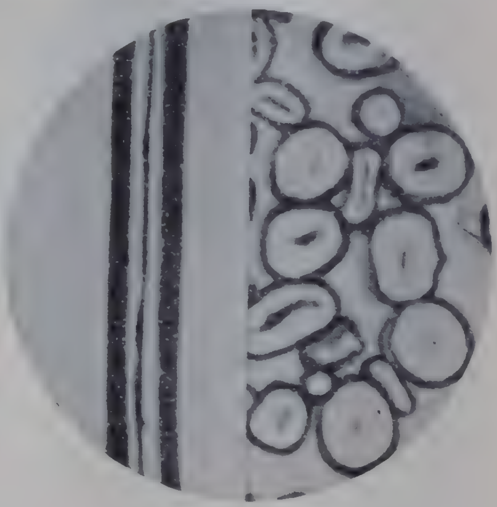
[60] Methods for the identification of textile fibers are fully described in (*a*) the 1949 Year Book of the American Association of Textile Chemists and Colorists; and (*b*) Tentative Textile Specifications, No. 13, 1948, *J. Textile Inst.* **39**, 51 (1948).

CHART 1

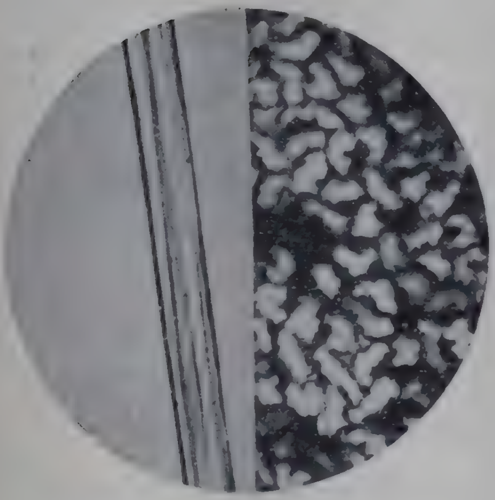
LONGITUDINAL AND CROSS-SECTIONAL MICROPHOTOGRAPHS OF TEXTILE FIBERS (×400)



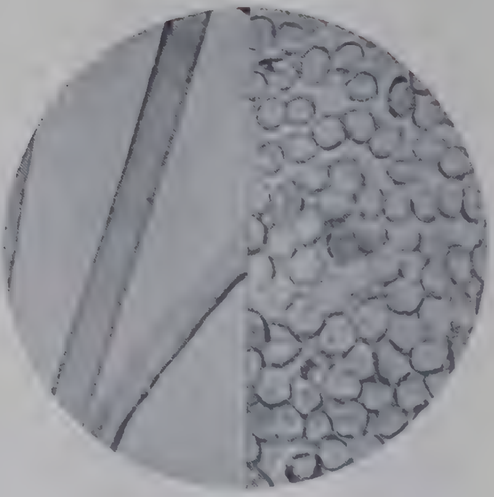
(1) Cotton



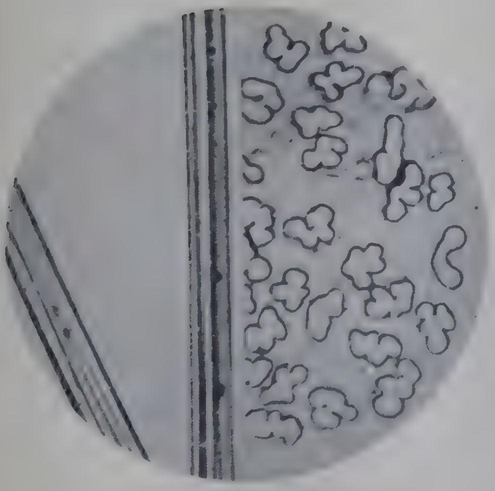
(2) Mercerized cotton



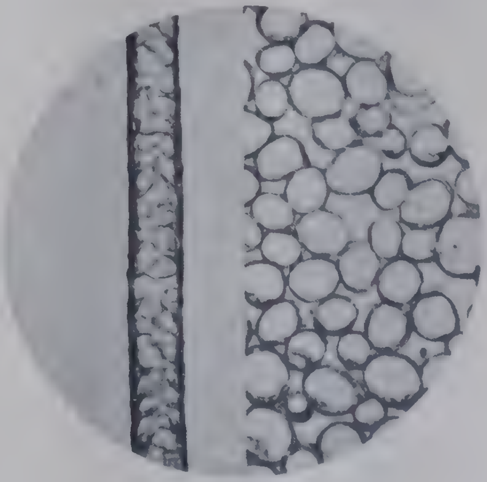
(3) Viscose



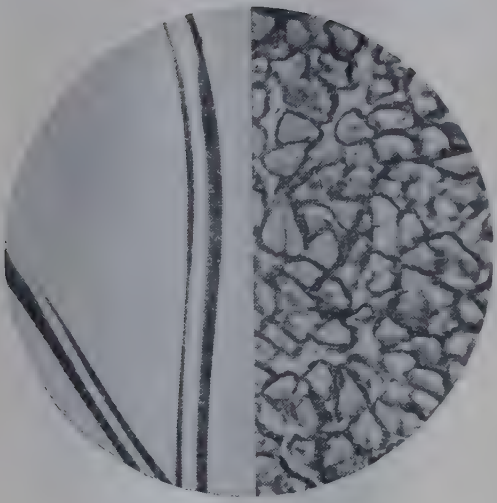
(4) Cuprammonium rayon



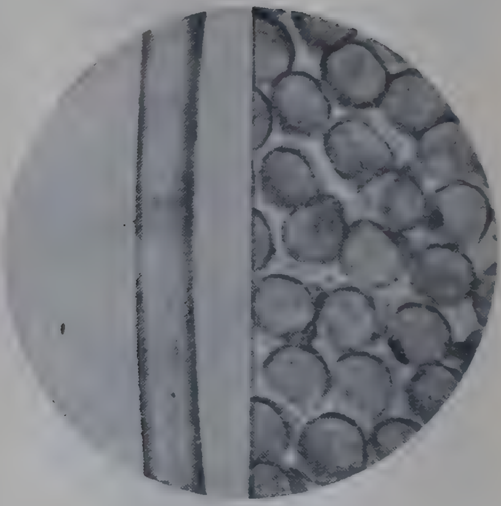
(5) Acetate rayon



(6) Wool



(7) Silk



(8) Nylon

Color reactions, as well as solubility and swelling tests, carried out with the aid of the microscope give a clearer indication than test tube reactions. Table I outlines a skeleton scheme for the identification of eight fibers in conjunction with the microscopic appearance. When other fibers are to be considered, and when mixtures of fibers which have been spun together and cannot be mechanically separated are involved, a much more complex scheme is necessary. Dyed fibers may have to be stripped before carrying out the color reactions.

DYES CLASSIFIED ACCORDING TO DYEING PROPERTIES

Dyes can be classified in accordance with their methods of application and their suitability for dyeing cotton and wool as representing the major fiber types. For the purpose of this classification, cotton includes other natural and regenerated cellulose fibers, and wool other protein fibers. The solubility of the dyes in water and in aqueous solutions of specific reagents, the presence of salt-forming groups, and certain constitutional factors are also involved in the dyeing classification.

Since the textile industry is interested in the dyeing properties of dyes, rather than their chemical constitution, dye manufacturers market their products under names which indicate the dyeing class, the shade, and sometimes other characteristics such as a notable fastness property, suitability for a special method of application, the concentration of the dye, and the physical form. For each dyeing class, every dye manufacturer has one or more special proprietary names, although for some of the old and well-known dyes (e.g., Congo Red, Sulfur Black) common names are used.

TABLE I

IDENTIFICATION OF SOME TEXTILE FIBERS

Test	*Cotton*	*Mercerized cotton*	*Viscose*	*Cuprammonium rayon*	*Acetate rayon*	*Silk*	*Wool*	*Nylon*
Burn	←Quick burning; smell of burning paper; acid vapors→				Burns with odor of acetic acid; black bead	←Slow burning with smell of burning hair; alk. vapors; bead formed		Burns with amide smell; round-head bead
5% Caustic soda solution	←Insoluble; structure retained→		←Slight yellowish color→		Swells slightly	Soluble hot	Soluble hot	Insoluble
80% Sulfuric acid	←Char and dissolve→					Soluble	Insoluble	Soluble
Concentrated hydrochloric acid	←No visible change→					Soluble	Insoluble	Soluble
Dilute HNO_3 (1:3)	←Unstained→					←Stained yellow→		Unstained
Ammoniacal copper solution	←Soluble→				Insoluble	Soluble	Swells, but insoluble	Insoluble
Acetone	←Insoluble→				Soluble	←Insoluble→		
90% Phenol	←Insoluble→				Soluble	Insoluble	Insoluble	Soluble
$ZnCl_2$-iodine[a]	←Reddish violet to blue→				Pale yellow	Yellow	Yellow	Yellow to brown
Malachite Green and Chlorazol Fast Red FS[b]	←Reddish violet→		Violet	Turbid red	Pale clear green	Dark blue	Green	Magenta
Stain X[c]	←Light blue→		Lavender	Dark blue	Pale greenish yellow	Brown-black	Yellow	Pale greenish yellow
Diazotized 5-nitro-*o*-anisidine[d]	←Unstained→					Champagne	Unstained	Unstained

[a] To a solution of zinc chloride (20 g.) in water (10 cc.), a solution of potassium iodide (2.1 g.) and iodine (0.1 g.) in water (5 cc.) is added.

[b] The fiber is treated with boiling 0.1% Malachite Green solution for 20 seconds, washed in warm water, treated for 20 seconds with boiling 0.1% Chlorazol Fast Red FS solution, and washed with cold water (Ref. 60b).

[c] Stain described by Davis *et al.*, *Ind. Eng. Chem. Anal. Ed.* **14**, 472 (1942). Composition: Acid Fuchsin (CI 692) (6 g.), picric acid (10 g.), tannic acid (10 g.), National Soluble Blue 2B Extra (CI 707) (5 g.), made up to 1 l. The fiber is immersed for 2 minutes in the cold, and rinsed.

[d] Immerse the fiber in a 5% solution of the diazonium salt neutralized to Congo Red with sodium acetate at 15-20° for 10 minutes; rinse and soap at the boil for 10 minutes with 0.2% soap solution.

Acid dyes dye wool from an acid bath, and they have little or no affinity for cotton. They constitute the most important group of dyes for wool and other protein fibers. Among the numerous dyes of this class, the fastness properties vary widely, but many dyes with excellent fastness are available. They are mainly sodium salts of sulfonic acids, and dyes of nearly every chemical class can in principle acquire the dyeing properties of acid dyes by the introduction of sulfonic groups. Thus there are acid dyes which are sulfonic acids of compounds belonging to the nitrophenol, azo, triphenylmethane, anthraquinone, indigoid, and other series; but in practice the great majority are azo and anthraquinone dyes. *Commercial names:* Amacid (AAP); Calcocid, Calcofast (AC); Acid, Cloth Fast, Benzyl, Kiton (Ciba); Anthraquinone, Anthracene (du Pont); Polar, Wool Fast (Gy); Acid, Coomassie, Carbolan, Disulphine, Lissamine, Naphthalene, Solway (ICI); Alizarin, Alphanol, Amido, Anthracene, Fast Acid, Naphthalene, Wool Fast (IG); Acid, Buffalo, Azo Wool (NAC); Acid, Alizarine, Sulphonine, Xylene (S).

Acid-mordant dyes are acid dyes with the additional property that their fixation on the fiber is improved by applying them in conjunction with metallic mordants, particularly chromium compounds, which are so generally employed for wool dyeing that these dyes are commonly known as chrome colors. A mordant is a substance or combination of substances which enables a dye to be fixed on a fiber. The mordant may be applied at various stages of the dyeing process. Water-soluble complexes of the dye and chromium can also be preformed (or prepared in substance instead of being produced on the fiber), and applied to the fiber by processes which enable a fiber-dye-metal combination to be effected. The groups which must be present in a dye to give it mordant-dyeing properties are indicated later in connection with the general class of mordant dyes. *Commercial names:* The term " chrome " usually occurs in the name, e.g., Chromoxane (IG); Eriochrome (Gy); Solochrome (ICI); but both acid and acid-mordant names are often included in the same group names, since there is no sharp line of demarcation between these two classes of dyes. Commercial names of metal complexes of acid-mordant dyes: Neolan (Ciba); Inochrome (Francolor); Ultralan (ICI); Palatine Fast (IG); Vitrolan (S).

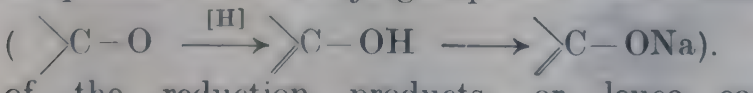
Basic dyes dye wool from a neutral or weakly acid bath, and they dye cotton mordanted with tannic acid and tartar emetic or with certain synthetic organic mordants. Basic dyes are ammonium, sulfonium, or oxonium salts; the usual acid components are hydrochloric, sulfuric, and oxalic acids, and the zinc chloride double salt of the dye chloride may be used. The basic nitrogen is in the form of primary or tertiary amino groups or a heterocyclic system; and just as sulfonation of dyes belonging to various chemical types yields acid dyes, basic dyes of different chemical classes may be obtained by the introduction of amino or dialkylamino groups and conversion into an ammonium salt. Heterocyclic systems (e.g., oxazine, thiazine) provide basic oxygen and sulfur. The basic dyes yield intense and brilliant shades, which unfortunately are fugitive to light and are therefore unsuitable for many purposes; but they are still valuable for certain styles of textile printing. *Commercial names:* Common names (e.g., Methyl Violet, Crystal Violet, Methylene Blue, Magenta, Rhodamine, Victoria Blue, Acridine Orange) are in general use.

Direct cotton dyes, as the name indicates, dye cotton directly. They are sometimes known as "salt dyes," since common salt (or Glauber's salt) is generally added to the dyebath for exhaustion; and some dyes in the absence of inorganic electrolytes have little or no affinity for cellulose. Direct dyes on cotton have poor fastness to washing, but the washing and light fastness can be somewhat improved by various aftertreatments on the fiber. Direct cotton dyes with excellent light fastness, which are either copper complexes or dioxazines, are now available. However, direct cotton dyes such as Congo Red with poor fastness properties continue to be used in very large quantities on account of the low cost of the dyes and the simplicity of the dyeing process. They dye wool and silk from a neutral or nearly neutral bath, and some have technical value for dyeing the animal fibers, especially silk from a soap bath. Like the acid dyes, they are sodium salts of sulfonic acids, but they are mainly azo dyes possessing specific structural features associated with substantivity for the cellulose fibers. *Commercial names:* "Direct" is in general use; Amanil (AAP); Calcodur, Calcomine (AC); Chlorantine (Ciba); Pontamine (du Pont); Diphenyl, Polyphenyl, Solophenyl (Gy); Chlorazol, Durazol, Icyl (ICI); Benzo, Chicago, Columbia, Diamine, Dianil, Mikado, Naphthamine, Oxamine, Oxydiamine, Pluto, Sirius, Stilbene, Toluylene (IG); Erie, Niagara, Solantine (NAC); Chloramine, Pyrazol, Solar, Trisulfon (S). The names often include "diazo", used for dyes suitable for diazotization and development, "cupra" (or similar indication), used for dyes which may be aftertreated with copper salts, and "form" (e.g., Benzoform, Plutoform, Erieform), used for dyes which can be aftertreated with formaldehyde.

Acid, basic and direct cotton dyes are all water-soluble.

Azoic dyes (ice colors; developed dyes) are a distinct class both chemically and from the dyeing point of view. They are insoluble azo dyes prepared on the fiber, especially cotton and other cellulose fibers, by impregnation with an alkaline solution of a coupling component, followed by development with a diazonium salt. β-Naphthol was the coupling component originally employed, but is now nearly obsolete because of the discovery of a series of much more useful substances which are mainly arylamides of 2-hydroxy-3-naphthoic acid. For dyeing and printing cotton in fast shades, the azoic dyes are next in importance only to the vat dyes, and they surpass the latter in the brilliance and solidity of the shades. These are marketed under such names as Naphtholate (AAP); Naphthosol (AC); Cibanaphtol (Ciba); Naphthanil (du Pont); Irganaphtol (Gy); Brenthol (ICI); Naphtol (IG); Naphthazole (Ku); and Celcot (S).

Mordant dyes have the property of combining with metallic hydroxides and salts to form complexes, sometimes called lakes, although lakes involve a substrate (e.g., a textile fiber). Many of the natural coloring matters (e.g., hydroxyanthraquinones, flavonols, and anthocyanins) have mordant dyeing properties. Various metals such as aluminium, chromium, iron, and tin may be employed, but there are preferences depending on the fiber and the chemical class of the dye. Dyes with mordant dyeing properties must contain groups capable of holding metals in stable combination, or chelate groups. Thus the dyes belong to four main types: (*a*) alizarin (1,2-dihydroxyanthraquinone) and its analogs; (*b*) *o,o′*-dihydroxyazo compounds; (*c*) azosalicylic acids; and (*d*) *o*-nitrosophenols or *o*-quinone monoximes. Chromium is the preferrred metal for dyeing wool and for printing cotton with mordant azo dyes ; aluminium for dyeing and printing cotton with alizarin; and iron for dyeing wool and printing cotton with *o*-nitrosophenols. Among the four types of mordant dyes mentioned, alizarin is the only dye of any importance for dyeing cotton, the well-known Turkey Red being for many years the fastest shade available for cotton. Alizarin is also a true mordant dye in the sense that it can only be fixed on a mordanted fiber, and is applied as a paste or suspension in water; for the unmordanted fiber it has no affinity. The *o,o′*-dihydroxyazo compounds and azosalicylic acids used technically contain, on the other hand, solubilizing groups, and they can be applied as acid dyes, the dyed wool fibers being treated subsequently or simultaneously with the mordant. This is also true of dyes of the alizarin type if they are sulfonated and thus rendered water-soluble, and these soluble mordant dyes have been classified earlier as acid-mordant dyes.

Vat dyes are insoluble in water, but give soluble sodium salts on treatment with caustic soda and a reducing agent, usually sodium hydrosulfite (hyposulfite; $Na_2S_2O_4$). This process of reduction and solubilization is known as "vatting." The chemical change in vatting is the reduction of quinone or carbonyl groups to alkali-soluble phenolic or enolic groups ( $\rangle C-O \xrightarrow{[H]} \rangle C-OH \longrightarrow \rangle C-ONa$). The vats or sodium salts of the reduction products, or leuco compounds, have affinity for textile fibers, especially cotton; and when the impregnated fiber is exposed to air the leuco compound is reoxidized to the insoluble parent dye. Vat dyes can be applied to wool, and find substantial use for silk; but it is necessary to keep the pH below a point at which damage to the protein fibers might occur. Vat dyes belong to two main chemical classes—indigoid and anthraquinonoid. The vat dyes as a class, especially the anthraquinonoids, are characterized by their high all-round fastness. The anthraquinonoid vat dyes represent the highest fastness to all agencies so far available among the synthetic dyes, and they are from this point of view the most valuable dyes for cotton. *Commercial names:* Amanthrene (AAP); Calcoloid, Calcosol (AC); Ciba, Cibanone, Dowanone (Ciba); Duraval, Leucosol, Ponsol, Sulfanthrene (du Pont); Solanthrene (Francolor); Tinon, Tinon Chlorine (Gy); Alizanthrene, Durindone, Caledon (ICI); Algol, Helindone, Indanthrene (IG); Carbanthrene (NAC); Vat (NAC and others), Sandothrene, Tetra (S).

Sulfurized vat dyes constitute a small group prepared by the sulfurization of certain indophenols and anthraquinone derivatives. Hydron Blue is the main example.

Solubilized vat dyes are soluble derivatives of vat dyes which have the requisite stability for storage in solid form. They are sodium salts of sulfuric esters of the leuco compounds ($\rangle$C-OSO$_3$Na). They have lower affinity for fibers than the alkaline vats. Like the parent vat dyes they are of two types—indigoid and anthraquinonoid. When the impregnated fiber is treated with an acid and an oxidizing agent, usually sulfuric acid and sodium nitrite, hydrolysis and oxidation to the parent vat dye take place. Since no alkali is involved, these solubilized vat dyes are as readily applicable to wool as to cotton, but in practice they are more extensively used for cotton dyeing and printing since cheaper and equally fast dyes are available for wool. *Commercial names:* Cibantine (Ciba); Tinosol (Gy); Soledon (ICI); Indigosol (DH; IG); Anthrasol (IG); Sandozol (S).

Sulfur (**or sulfide**) **dyes**, like the vat dyes, are usually insoluble in water and form soluble sodium salts on reduction under alkaline conditions. Sodium sulfide is the reagent employed for the dual purpose. The dyeing is carried out from a hot sodium sulfide bath, and the parent dye regenerated on the fiber by exposure to air. Enormous quantities of Sulfur Black are used for dyeing cotton, and among the numerous synthetic dyes, Sulfur Black occupies the first place in the figures for production. Sulfur Blues and Greens are also widely used. The sulfur dyes on cotton have good fastness to light and washing, but their disadvantage is the poor fastness to chlorine. A few sulfur blacks and greens with improved fastness to chlorine, however, have been produced in recent years. Sulfur dyes are normally applicable only to cotton, since wool is damaged by sodium sulfide. Special methods for dyeing wool are known, but are of little practical interest. Chemically, the sulfide dyes are characterized by a common method of preparation which consists in heating certain intermediates with sulfur or sodium sulfide or polysulfide. Sulfur dyes are indicated by "Sulph," "Thio," "gen," or "gene" in the *commercial names*. Examples are Calcogene (AC); Pyrogene, Thiophenol (Ciba); Sulfogene (du Pont); Katigen (Gy); Thionol (ICI); Sulfindone (NAC). Immedial (IG), Indo Carbon (IG), and Eclipse (Gy) are also sulfur dyes.

Oxidation colors, like the azoic dyes, are produced on the fiber, but they are classified separately since their method of application is distinct. The only important example is Aniline Black, which is produced by impregnating cotton with aniline hydrochloride, and oxidizing it on the fiber by various methods to a fast black dye, probably constituted as a complex azine. For the oxidation an oxidizing agent such as sodium chlorate is used in conjunction with an oxygen carrier such as copper sulfate. Aniline Black is largely used in cotton dyeing and printing, but it is valueless for wool. The oxidation of *p*-phenylenediamine, *p*-aminophenol, and other amines is utilized for dyeing fur.

Cellulose acetate dyes. While the dyes belonging to all the dyeing classes described so far are applied from an aqueous solution or produced as insoluble pigments by chemical reactions carried out on the fiber, a method developed for dyeing cellulose acetate rayon, which does not absorb the usual cotton dyes, is the use of aqueous dispersions of colored compounds, which are insoluble or sparingly soluble in water. Chemically, cellulose acetate dyes are relatively simple aminoazo compounds and aminoanthraquinone derivatives, usually containing ethanolamine ($-NHCH_2CH_2OH$) and similar groups which render them more readily dispersible in water and also facilitate their absorption by cellulose acetate. More recently the same types of compounds have also been found to dye cellulose acetate when they are used in the form of the water-soluble sodium salts of the half esters with sulfuric acid (compounds of the type $ArNHCH_2CH_2OSO_3Na$). *Commercial names:* Cellulose acetate dyes usually include "acet" or "cel" (from Celanese) in the name; e.g., Cibacete (Ciba); Celanthrene (du Pont); Setacyl (Gy); Solacet (ICI); Celliton (IG). Calconese (AC), Duranol (ICI), Dispersol (ICI), and Artisil (S) are also acetate rayon dyes.

Dispersed dyes. Multiphase dispersions of pigments, resins, and water can be used for textile printing, and such dispersions are also finding use in dyeing, or, more strictly, all-over coloration. For cellulose acetate the use of aqueous dispersions is based on the solubility of the organic pigments in the fiber, but for dyeing and printing cotton the impregnation is mechanical and the pigment is then fixed on the fiber by resin bonding. A variation is to apply a dyestuff to a solid cellulose ether (e.g., hydroxyethylcellulose), dissolve the dyed ether in aqueous alkali, dye a cotton fabric with this solution and precipitate the dyed ether with acid.[61]

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[61] Carroll and Dan River Mills, USP 2,448,515; see also Edelstein, USP 2,442,972.

Mineral colors. Although this book is concerned with the organic coloring matters, it is necessary to mention in passing that inorganic substances have been extensively used in the past and find limited use even at the present time for dyeing and printing. For nontextile coloration purposes, mineral colors continue to be predominantly important on account of their low cost and stability in comparison with the organic coloring matters. The chief example of an inorganic pigment used for a dyeing process is mineral khaki, produced on cotton fabrics (particularly military uniforms) by impregnation with a solution of iron and chromium salts, followed by precipitation of the mixed hydroxides on the fiber by alkaline and ageing treatments. Chrome yellow and orange, iron buff, Prussian Blue, and manganese brown are other examples of mineral colors. The mineral pigments still have a definite place in calico printing, and they are applied with albumin as fixing agent or in the form of dispersions in resins.

PREPARATION FOR DYEING

Prior to dyeing it is necessary to give the fiber a wetting out or scouring treatment, so that the dye liquor may penetrate the fibrous material thoroughly and produce level dyeing. Scouring and other preparatory treatments applicable to cotton, wool, silk, and other fibers have been indicated earlier, and pretreatment for dyeing depends on various factors such as the nature of the fiber and the form in which it is used, the depth of the shade, and the subsequent processing to which the dyed material is to be submitted. Cotton hanks and pieces may be kierboiled with alkali and soap, and given a full bleach, if pale shades are to be dyed. Cotton piece-goods, particularly cloth to be printed, may be singed to produce a smooth surface, i.e., passed rapidly through a gas flame so that the neps and protruding fibers are burnt off, before kierboiling; the singeing may be carried out on one side or on both sides of the fabric. If cops or cheeses are to be dyed in a package dyeing machine, the material[62] is merely treated with a warm solution of a wetting agent, which is then withdrawn and replaced by the dye liquor.

With a given fiber the choice of a dyestuff of a particular dyeing class is governed mainly by considerations of the fastness required and of the cost. Thus for cotton yarn which has to be dyed and subsequently kierboiled and bleached in the piece, only two groups of dyes can be used—the azoics and the anthraquinonoid vat dyes, adding a few indigoid dyes to the latter group.

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[62] The "material" in dyeing practice refers to the textile material in whatever form it may be used.

Dyed shades must usually conform exactly to given samples, and shade matching calls for great skill. Shades are matched visually in ordinary practice, and the accuracy of a competent dyer is remarkable; spectrophotometric methods are useful for laboratory control. The recipe is first set by an experimental dyeing carried out with a small skein or a few square inches of fabric; porcelain dye-pots, conical in shape so as to enable 100 cc. or less of dye liquor to be conveniently handled, are employed, and the material is turned in the dyebath by means of a glass rod. The weight of dye in proportion to the weight of the material represents the percentage of the shade; thus a 2% shade means that 2 g. of dye has been used for 100 g. of the material. The volume of the dyebath in relation to the weight of material is known as the length of the liquor or bath. In some dyeing processes the bath is almost completely exhausted so that the amount of dye taken determines the strength of the shade; but in other cases (e.g., Indigosols and Soledons; " naphthols "; padding processes in general) shade calculations have to be based on the initial concentration of the dye (in grams per liter or pounds per 100 gals.) in the dyebath. It is obviously an advantage if the required shade can be matched by using a single dye (a " self shade "). While a commercial dyestuff may itself be a mixture of two or more dyes, a reputable dye manufacturer will only mix dyes with as similar solubility, rate of absorption, levelling power, and fastness as possible; and if the dyer has to dye compound shades he must choose for admixture such dyes as have closely similar dyeing and fastness properties. Experimental dyeings are of value in determining the dye or combination of dyes to be used, but the other factors such as the quantity of dye, the length of liquor and the time of dyeing have to be varied in the light of experience in large scale dyeing and with reference especially to the type of machine.

Dyeing processes for the various fibers are briefly outlined below. The shade cards, pamphlets, and manuals issued by dye manufacturers provide invaluable guidance; with a given dye, the conditions of dyeing exert a vital influence on the depth, evenness, and fastness of the dyeing, and the dye manufacturer therefore attempts to give all the assistance that he can.

Water is the universal medium in which dyeing is carried out, and it is desirable to use as pure water as possible, cost being the only limiting factor since the dyer employs very large volumes. Among the objectionable impurities are iron, calcium, magnesium, and other metals which form precipitates with dyes and with the reagents (e.g., soap and alkali) employed in dyeing and related operations. Softening the water by an inexpensive procedure is therefore common practice.

COTTON DYEING

As stated earlier, cotton may be dyed in various forms. Cloth, other than knitted fabrics and nets, are treated in open width. Shorter baths and relatively higher concentrations of dyes and reagents calculated on the volume of the liquor are used in machine dyeing than in open beck dyeing. Mercerized cotton requires special care in dyeing because of the increased affinity for dyes and the danger of unlevel dyeing.

Direct dyes. The material-liquor ratio may vary from 1:5 to 1:20, shorter baths being in general preferable. Standing baths (i.e., the exhaust liquors from previous dyeings) can be employed for heavy shades. Dyeing is usually carried out at or near the boiling point, but temperatures as low as 40–50° are suitable in some cases. Building up of the shade and exhaustion of the dye are effected by the addition of common salt (10–30% or more of the weight of the material) or Glauber's salt, the latter being preferable for lighter shades. For dyes which are not very readily soluble and for dyes sensitive to acids (e.g., Congo Red), soda ash may be added; disodium hydrogen phosphate gives good exhaustion and level dyeing. Sulfonated oils are useful additions for improving penetration and brightness. After dyeing the material is rinsed cold and dried. From an examination of a series of direct cotton dyes, a Committee of the Society of Dyers and Colourists conclude that their behavior can generally be defined in terms of migration, salt controllability (as distinct from salt sensitivity), and the influence of temperature and liquor ratio on exhaustion. Giving the results of the evaluation of 45 dyes and a list of standard dyes for comparison, direct dyes have been classified into (*a*) self-levelling, (*b*) salt-controllable and (*c*) temperature-controllable. Levelling and salt controllability tests are described.[63]

The aftertreatment of direct dyes on the fiber by diazotization and development, by coupling with diazonium salts, and by means of formaldehyde, copper sulfate, and potassium dichromate, and certain quaternary ammonium salts, is discussed fully in Chapter XVII. Direct dyed shades may be " topped " with basic dyes, of which a very small amount (about 0.05% on the weight of material) is sufficient, to increase the brightness; the direct dye acts as a mordant for the basic dye, or a treatment with tannin and tartar emetic may be interposed.

Azoic dyes. There are two distinct stages in the dyeing process: (1) impregnation with an alkaline solution of a coupling component; and (2) development with a diazonium salt. The Naphtol (Brenthol or other equivalent) is dissolved in caustic soda solution with the addition of alcohol or a wetting and dispersing agent, if necessary; it is possible to dissolve in the cold in the first case, but the mixture has to be boiled if alcohol is not used. After cooling to about 50°, 40% formaldehyde (equal in weight to the Naphtol) is added (for exceptions see Chapter XXII). The material is now impregnated for a few seconds to an hour depending on the type of equipment employed; the temperature is 30–40°, except in the treatment of cloth on a padding machine, when the temperature is just below the boiling point. Yarn is then hydroextracted (i.e., worked in a centrifuge for removing excess liquor as far as possible), while padded cloth is dried on steam-heated copper cylinders or in a hot flue drier. The developing bath is prepared by diazotizing a Fast Color Base (a primary aromatic amine suitable for azoic dyeing) by means of sodium nitrite and hydrochloric acid or by merely dissolving a Fast Color Salt, which is a stabilized diazonium salt. The pH is controlled by the addition of a substance such as sodium acetate or basic aluminium sulfate; and other usual additions are a protective colloid (e.g., Diazopon A, IG; Azopol A, ICI) and common salt. The " naphtholated " material is now worked in the diazonium liquor until coupling is complete. The dyed material is finally rinsed with weak hydrochloric acid and with water, and given a vigorous treatment with a boiling solution of about 0.2% soda ash and 0.3% soap for 30 minutes, followed by a thorough rinse with hot water. Good fastness to rubbing partly depends on the efficiency of this aftertreatment.

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[63] *J. Soc. Dyers Colourists* **62**, 280 (1946); **64**, 145 (1948).

Basic dyes. Yarn is first mordanted with tannic acid (1–6% on weight of material) by working in a solution (length of liquor 1:10) at 70–80° for 1 hour, and in the cooling bath for 3–4 hours, and then steeping overnight. After hydroextraction, the material is treated in a cold bath of tartar emetic (half the concentration of the tannic acid) for 20–30 minutes, and rinsed in cold water. An alternative method of mordanting is to use synthetic mordanting agents such as Katanol ON (IG) or Taninol BMN (ICI); the advantages are that the mordanting involves only a single treatment and the shades are somewhat brighter and faster to washing, but the low light fastness of the basic dyes is in some cases still lower when a Katanol mordant is used. The synthetic mordanting agents have therefore very limited application for a few dyes such as Auramine O and some of the Rhodamines and Safranines. Katanol (3–6% on weight of material) and soda ash (2–3%) are dissolved in water, and while working the material in the liquor at 60–70° common salt (20–40%) is added in the course of an hour. Mordanted by either method, the material is then dyed in a bath made up with 2–3% acetic acid or alum, first at room temperature and finally at about 60°. A second treatment with tannic acid and tartar emetic (" back tanning ") improves the fastness to washing, but the brightness is impaired. Aftertreatment with about 2% Auxanine B (IG), a phosphotungstomolybdic acid, in presence of common salt and acetic acid, improves the fastness to light.

Mordant dyes. The only dye of any importance is Alizarin for Turkey Red, the fast fiery red shade being still valued in India and China. A serious disadvantage is the length of the process, which takes a minimum of three days; the older processes, claimed to give faster shades, took several weeks. Yarn is first oiled with a 10% solution of Turkey Red oil (sulfated castor oil), dried at 65°, and the process repeated. The next stage is mordanting with aluminium sulfate (which must be completely free from iron), soda ash and chalk, neutralized with acetic acid, by impregnation in the solution overnight at 30°. Fixation with a weak solution of sodium phosphate follows, and the material is then dyed by working in an 8% suspension of Alizarin in water containing Turkey Red oil, first in the cold and finally at a temperature of 90°. The yarn is then steamed at 15–20 lbs. pressure and soaped. Attempts to shorten the application of Turkey Red have been described from time to time.[64]

Vat dyes. The anthraquinonoids are mainly used. The dyebath is prepared by adding the dye, pasted with water and a dispersing agent if necessary, to water containing the requisite amount of caustic soda and hydrosulfite. IG divide the anthraquinone vat dyes into three dyeing classes (IK, IW, and IN), depending on the amount of caustic soda used in vatting which varies from 0.1 to 0.5% on the volume of the dyebath, and on the temperature of dyeing which varies from about 20° to 60°. The length of the liquor is 1:20 for open beck dyeing, and 1:10 for dyeing in package machines, and in the latter case the concentration of the reagents has to be increased by about 50%. Dyeing is commenced when a clear vat has been obtained, and since alkali and hydrosulfite are consumed by absorption of atmospheric oxygen, the presence of an excess of alkaline reducing agent is tested for by means of vat paper (paper impregnated with Flavanthrone, a yellow dye which gives a blue vat), and more alkali and hydrosulfite are added as required. The hydroxyl ion concentration influences the color value obtained from a given dye, and this factor must be carefully controlled. Mixtures of vat dyes are especially difficult to handle, and vat dyeing as a class needs high manipulative skill based on a study of the properties of the individual dyes in the series. The IK and IW colors require common salt for exhaustion. After impregnation the material is squeezed to remove excess dye liquor, and oxidation is effected by exposure to air. In machine dyeing oxidation may be accelerated by treating the impregnated material, after a short rinse, with water containing about 0.05% potassium dichromate and 0.1% sulfuric acid or about 0.2% sodium perborate. As with the azoic dyes, the true shade and the maximum fastness to light and rubbing are only obtained by vigorous soaping of the dyed material. The application of the anthraquinonoid vat dyes is discussed further in Chapter XXX.

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[64] Cf. Haller, *Helv. Chim. Acta* **23**, 466 (1940).

Solubilized vat dyes (Indigosols; Soledons). The chief use of the Indigosols and Soledons is for dyeing pale shades on cotton fabrics (jigger or padding machine). The dyebath is prepared by dissolving the dye, Glauber's salt (15–120 times the weight of the dye) and sodium nitrite (2–16 parts) in water, and the impregnation is carried out at 40–80° in as short a liquor as possible. The material is then squeezed and developed by passage through a 2–4% solution of sulfuric acid at about 60°. In view of the danger of degradation of cellulose by the combined action of an oxidizing agent and mineral acid, the dyed material is immediately treated with a solution of soda ash, rinsed, and soaped at the boil.

Sulfur dyes. The dyebath is prepared by pasting the dye with soda ash solution, adding sodium sulfide (1–3 parts for one of dyestuff), followed by 10–20 times the quantity of boiling water, and boiling until a clear solution is obtained. Dyeing is usually carried out at the boil, but a temperature of 50–60° is recommended for some of the blue and green dyes. As the dyeing proceeds, there must be enough sodium sulfide to keep the dyestuff in solution, but a large excess retards the absorption. The alkalinity of the bath should be maintained by the addition of soda ash (1–10% on the weight of the material). As with the direct cotton dyes, common salt (5–40% on the weight of the material) is necessary for exhaustion. Since sulfur dyebaths cannot be exhausted completely except by adding excessive amounts of salt resulting in bronzy dyeings, it is common practice, for instance in dyeing Sulfur Black, to use standing baths. The dyed material is squeezed, and thoroughly rinsed with water till the washings run clear and nearly colorless. Any aftertreatment is usually unnecessary, but hot soaping or treatment at about 70° with an emulsion of a vegetable oil and a sulfated oil brightens the shade and gives a softer handle. Sulfur Blue shades are improved in brightness by an aftertreatment with sodium perborate, but the light fastness is decreased. Topping with basic dyes or with Aniline Black is also used occasionally. Sulfur Black is dyed on cotton in all forms, and in especially large quantities on loose cotton for admixture with wool and shoddy.

DYEING OF VISCOSE AND CUPRAMMONIUM RAYON

One of the precautions for avoiding mechanical damage to the delicate fibers is to dye as rapidly as possible. For hank dyeing the use of specially designed machines is common practice; and rayon fabrics are conveniently treated on a winch like wool and silk.

The usual pretreatment for removing oils, gelatine and other sizing materials is to scour at about 95° with a solution of soap and soda ash (for viscose) or ammonia (for cuprammonium rayon).

Direct cotton dyes are largely used, a selected range of level dyeing colors being recommended by dye manufacturers. Rapid dyeing dyes are the best.[10] Dyeing is commenced just below the boiling point, and level dyeing is facilitated by the addition of soap or a sulfated oil (e.g., Monopole soap). The use of salt for exhaustion is preferably avoided, or at least kept to a minimum, particularly for cuprammonium rayon, which has an even higher affinity for dyes than viscose.

Azoic dyes. The full range is applicable to viscose, but there are certain differences in comparison with cotton dyeing. Lower concentrations of both the Naphtol and the diazonium solutions have to be employed. Hydroextraction after impregnation is replaced by a rinse with common salt solution containing a little caustic soda. Soaping is carried out at 50–60° for some dyes, since " blinding " of the luster occurs at the boil by the crystallization of the pigment in large aggregates; soap may be replaced by a synthetic detergent such as sodium lauryl sulfate.

Basic dyes. The danger of unlevel dyeing is least with the basic colors. Pale shades can be dyed without a mordant, but the fastness to washing and light is naturally very poor. The mordant dyeing methods are similar to those described for cotton, and a notable fact is the higher fastness exhibited by some basic dyes on viscose.

Vat dyes, together with the Indigosols and Soledons, are as important in dyeing viscose as in dyeing cotton because of the excellent, all-round fastness of the shades.

Sulfur dyes are of limited application, since none is available which is capable of covering the heterogeneous dyeing properties of rayon like many of the direct cotton dyes.

Acid dyes. Viscose and cuprammonium rayons can be printed with acid dyes with urea in the thickening for improved solubility. Dyes of large particle size have to be used, and steaming is necessary after printing and drying. Under these conditions the dyes penetrate the fiber and are fixed by subsequent aggregation within the fiber.[65]

DYEING OF ACETATE RAYON[8]

Acetate rayon fabrics are desized[10] by padding with an emulsion of xylene in ammonia and Monopole soap solution at 60–80°, and piling for a few hours. They are then scoured with a solution of about 0.2% soap and 0.1% ammonia at the same temperature for one hour. If the rayon is to be delustered, a treatment with a solution of 2% olive oil soap and about 0.25% phenol at 100° for 30 minutes is given; after a final rinsing with 0.25% aqueous ammonia and then with water, the material may be dyed. The dispersed dye is made up to the desired volume with water containing soap or a synthetic wetting agent. Dyeing is carried out by working the material in this dyebath at 80–85°, the fiber taking up the dye substantially in the same manner as an organic solvent. No additions are necessary for exhausting the dyebath, and fast level shades are obtainable. Dyes with a readily diazotizable amino group may be diazotized on the fiber and developed with a coupling component such as 2-hydroxy-3-naphthoic acid for producing black shades, For diazotization a solution containing 0.15% sodium nitrite and 0.45% hydrochloric acid is used; the developing bath is prepared by dissolving hydroxynaphthoic acid in sodium carbonate solution and then acidifying with acetic acid. After working the diazotized material in this solution for a few minutes at room temperature, the temperature is kept at 60° for 30 minutes.

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[10] See p. 256.

[65] Meitner, ICI Technical Monograph No. 2.

[8] See p. 254.

Water-soluble dyes (Solacet dyes, ICI, 1935), which are applied to acetate rayon by the same method as direct cotton dyes for cotton, are now available. They give better penetration and more level shades than the dispersed dyes, and are therefore useful in dealing with tightly woven materials.

WOOL DYEING[65a]

Scouring with a liquor containing about 0.75% soap and 0.25% soda ash (or potassium carbonate or ammonia) at 50–60° is the usual preparation of loose wool for dyeing; countercurrent washing in a series of bowls with decreasing concentration of the reagents is common practice. Slubbing is dyed "in the oil" (about 3% of a nondrying vegetable oil or synthetic lubricant used in the combing processes). Yarns and fabrics are subjected to a thorough cleansing with soap and/or soda ash or a synthetic detergent, and in some cases they are also bleached by means of sulfur dioxide or hydrogen peroxide.

Loose wool and yarns may be dyed in open becks or a Hussong machine or package dyeing machines. Tops are dyed in the can, Hussong, or Abbott type machines. For piece dyeing the winch is invariably employed.

Acid dyes. The bulk of wool dyeing is carried out with acid dyes, the advantages being the simplicity of the dyeing process, the brightness of the shades, and the relatively low cost of the dyes. They are dyed from an acid bath, and the cheapest acid, sulfuric acid (3–4% on the weight of the material), is adequate for the level dyeing dyestuffs; Glauber's salt

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[65a] Bird, The Theory and Practice of Wool Dyeing, Society of Dyers and Colourists, 1947.

(10–20%) is a useful addition for restraining the absorption and producing level shades. Formic acid is preferred for dyeing fabrics containing cellulose fibers, and acetic acid for dyes with poor levelling properties and for materials which do not readily absorb the dye liquor. Level dyeing is further facilitated by the use of ammonium sulfate or acetate instead of an acid; the ammonium salts liberate acid slowly in the dyebath at the boil with consequent slow exhaustion and even dyeing.

The dyebath is set by dissolving the dye in boiling water and adding the requisite amount of acid. Dyeing is carried out at the boil until the desired shade is obtained, but the temperature at which the material is introduced into the dye liquor, the rate at which the liquor is raised to the boil, and the addition of acid, Glauber's salt, etc., are subject to wide variation in accordance with the properties of the dye and of the material. Acid dyes belong to two broad classes: (1) dyes which yield level shades from a sulfuric acid-Glauber's salt bath by virtue of their ability to migrate at the boil; the wet fastness is poor; and (2) dyes forming large aggregates in solution and with bad levelling properties; these have to be dyed from a weakly acid (such as an ammonium acetate) bath, and the temperature must be raised gradually; but the shades have good fastness to wet treatments. An intermediate type is represented by dyes which are dyed from a weakly acid bath, but exhausted with sulfuric acid. Some of the direct cotton dyes are to be grouped among the acid dyes applied from an acetic or formic acid or ammonium acetate bath. A little sodium dichromate prevents the decomposition of certain dyes (Sulphon Cyanine or Coomassie Navy Blue type) and improves the fastness of the shades.

Chrome complexes of acid-mordant dyes (Palatine Fast and Neolan types). These are dyed like the acid colors from a sulfuric acid bath, but are similar to the chrome colors in their fastness properties. Dyeing is carried out at the boil in a bath containing 5–10% sulfuric acid. After dyeing the material is thoroughly rinsed, and addition of sodium acetate or ammonia to the last rinsing bath is desirable.

Chrome dyes. Mordanting may be carried out (*a*) before dyeing (on-chrome process), (*b*) after dyeing (after-chrome process), and (*c*) during dyeing (metachrome, monochrome or chromate process). (*a*) The first and oldest method is now used only to a limited extent. The mordanting agent is sodium dichromate (2–4% on the weight of the wool); the material is entered into the liquor at 50°, and treated at the boil for 1-1½ hours. Wool is thus colored yellow, and the mordant which is almost entirely in the oxidized condition has an oxidizing action on the dye. If this is undesirable, a "green mordant" is produced by the addition of tartar (acid potassium tartrate) or oxalic, lactic, or formic acid to the dichromate so that reduction to green chromium hydroxide takes place. The mordanted wool is rinsed and dyed from an acetic acid bath, first in the cold and finally at the boil. (*b*) The afterchrome process is largely used, specially for heavy shades of brown, blue and black; it is more economical than the on-chrome process and the shades are faster. The material is first dyed from a Glauber's salt-acetic acid bath, exhausted if necessary by the addition of sulfuric acid or formic acid. When the bath is completely exhausted, sodium dichromate (1–2%) is added and boiling continued for 30 minutes to 1 hour. The wool is then rinsed off quickly. With many of the acid-mordant dyes, e.g., the Chromotropes, a profound alteration in shade takes place on chroming. (*c*) Unlike the first two methods, the metachrome or chromate process is a single bath process, and it is particularly valuable for light and medium shades. Matching to shade is easier by the metachrome process, since level dyeing acid colors unaffected by chromium compounds can be used for the purpose. The metachrome process is only applicable to certain dyes, but the range is now quite extensive. The process consists in dissolving the dye in boiling water, adding the metachrome mordant (sodium chromate and ammonium sulfate), and dyeing at the boil for an hour or more. Additions of Glauber's salt, acetic acid, or ammonium acetate may be made. The dye, which is not precipitated by chromate, forms an insoluble lake on the fiber by the gradual liberation of acid from the ammonium salt and the conversion of chromate to dichromate.[66] Race has studied the relation between the rate of formation of the chromium complexes of a dye and its value in the metachrome process.[66a]

In the "calcomet" process[67] dyeing is accomplished in a bath which initially has a $pH > 7$ by using an optimum low amount of dichromate, magnesium sulfate, and a surface-active agent as a dyeing assistant. The addition of magnesium sulfate to the alkaline dyebath results in the formation of a magnesium dye complex without appreciably affecting the pH. Below pH 7 the magnesium complex appears to be unstable. By this method wool can be successfully dyed with chromable dyes which are not usually applied by the metachrome method.

Basic dyes. A few, such as Victoria Blue, are employed for the brilliance of the shades and their good fastness to washing, in spite of the poor fastness to light. No addition to the dyebath is normally necessary, but soap for increasing the brightness or acetic acid for assisting level dyeing may be added. Dyeing is commenced in the cold and completed at 90–95°.

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[66] See also Peryman, *J. Soc. Dyers Colourists* **64**, 283 (1948).

[66a] *J. Soc. Dyers Colourists* **66**, 141 (1950).

[67] Royer, Millson and Amick, *ibid.* **63**, 214 (1947); see also Millson, Royer, and American Cyanamid, USP 2,443,166.

Vat dyes. Indigo is important for wool dyeing, although its use is steadily declining. The old fermentation vat, in which fermented woad, suint from raw wool, and other natural products are used for the reduction, is now little used; and the hydrosulfite-ammonia vat is generally employed. The dye is first vatted in a concentrated solution using caustic soda and hydrosulfite (stock vat process), or it may be used as indigo white (leuco-indigo) containing a small amount of caustic soda, one of the forms in which indigo is marketed. The dyebath is set with about 3% glue, 1–3% of 25% ammonia, and 2% hydrosulfite, and the stock vat is then added. Dyeing is carried out at 50–55° for 20–30 minutes, the material being then squeezed and allowed to stand for oxidation of the leuco compound. For deep shades the impregnation (or dip) and oxidation may be repeated. "Indigo blue" shades are often obtained on worsteds by dyeing a light or medium shade with indigo, and then producing a full shade by means of an acid or chrome blue. Other indigoid and thioindigoid dyes are applied similarly.

Solubilized vat dyes. The Indigosols and Soledons are first applied like acid colors from a bath containing acetic acid or ammonium sulfate, commencing the dyeing at 40° and boiling for 30 minutes to an hour. The material is then rinsed, and developed in a bath containing 1–2% ammonium sulfocyanide, 0.7–3.5% sodium dichromate and 2% sulfuric acid (all on the weight of the material) at 85–90° for one hour. Ammonium sulfocyanide prevents overoxidation of the dyes. A few of the Indigosols (Indigosol O, OR and Green IBA) are developed cold with sodium nitrite and sulfuric acid. The dyed material is finally rinsed with soda ash solution and with water.

SILK DYEING

Although silk, as a protein fiber, has affinity for the same classes of dyes as wool, there are differences in dyeing practice. These are due to (*a*) the need for avoiding friction so as to maintain the full luster, (*b*) the high cost of the fiber which justifies the use of expensive dyes to obtain maximum fastness, and (*c*) the greater stability of silk to the action of caustic soda. The forms in which silk comes for dyeing are yarn (as hanks), fabrics, and knitted goods. Hanks are dyed by hand or in the type of machine used for rayon; sticks and rollers are made of glass, porcelain, or stainless steel. Pieces are dyed on the winch. Silk which has been degummed by the usual process of treating with a solution of soap (25–30% on the weight of the material) at 90–95° for 2 hours requires no further preparation for dyeing dark shades; but for pale shades, a second soaping with 15% soap may be given. Boiled-off liquor "broken" with acetic or sulfuric acid gives an emulsion of fatty acid and silk gum, which may be added to the dyebath (a third of the volume) as a levelling agent.

Direct cotton dyes. Many direct cotton dyes, applied from a neutral bath, yield shades with good fastness to light and washing. A few are better applied like acid colors from an acetic or formic acid bath. The temperature of dyeing is about 90°, and methods of aftertreatment such as diazotization and development may be used for modifying the shades (specially for producing deep reds and blacks) and improving the fastness.

Acid dyes are largely used. They are applied from an acetic acid or sulfuric acid bath, or from a neutral bath in which Glauber's salt is used for exhaustion. Dyeing is commenced at 40–50° and completed at 90–95°. The neutral dyeing dyes give excellent results, especially on tin-weighted silk for which the dyes requiring sulfuric acid are unsuitable since they have little or no affinity and sulfuric acid acts on the tin salts.

Mordant dyes (e.g., Alizarin Orange and Gallein) are useful for dyeing silk, if mordanting is carried out under conditions which leave the luster unimpaired. In contrast with wool dyeing, the premordanting method is preferred to the metachrome and afterchrome processes, and both aluminium and chromium mordants are used. Thus silk yarn may be soaked in a cold solution of basic aluminium sulfate or of chrome alum, and the mordant fixed by means of sodium silicate.

Basic dyes are useful for silk when brilliant shades are desired and light fastness is not important. The fastness to washing may be improved by an aftertreatment with tannin and tartar emetic.

Vat dyes are more extensively used for silk (unweighted yarn) than for wool. The concentrations of caustic soda necessary for dyeing the anthraquinonoid vats can be employed, if glue is added, the temperature is kept below 50°, and relatively large amounts of common or Glauber's salt are employed for exhausting the dyebath in view of the poor substantivity of the leuco compounds for silk. The indigoids are easier to dye because of their higher substantivity and the lower concentrations of caustic soda involved, but the anthraquinonoid vat dyes are being increasingly used in view of their superior fastness. Since the vat dyes are fast to the degumming process, raw silk can be dyed, woven into fabric, and degummed at a later stage.

Solubilized vat dyes. The Indigosol or Soledon is applied from a bath containing formaldehyde-sulfoxylate (Rongalite; Formosul) and acetic acid, first in the cold and finally at 90°; formic acid is used for exhaustion. The material is then rinsed and developed as described for wool. An alternative method is to pad the fabric in a liquor containing the dye, thiodiglycol, sodium chlorate, ammonium thiocyanate, ammonium vanadate, and a wetting agent; then dry, steam for about thirty minutes, wash and soap.

NYLON DYEING

Acetate rayon dyes are applied to nylon from a soap bath at 85–90° for 1 hour, and they have good levelling properties. The shades differ in many cases from those on acetate rayon,[68] and the affinity for nylon is considerably lower. The shades on nylon generally have inferior light fastness and superior washing fastness. The diazotized and developed blacks can be dyed on nylon, but the concentration of sodium nitrite and hydrochloric acid used for acetate rayon must be doubled. Mixtures of dyes have to be carefully chosen after a study of the individual rates of dyeing, temperature range, and migration properties.[69] The Solacets have excellent affinity for nylon.

The acid dyes have not proved very satisfactory in practice, particularly when mixtures of dyes have to be used. The level dyeing dyes, applied from a formic or acetic acid bath at 80–90°, without the addition of Glauber's salt or sulfuric acid, give reasonably good results in pale and medium shades.[70] Some acid dyes and direct cotton dyes exhibit higher wet fastness on nylon than they do on wool or cotton.

JUTE DYEING

For dyeing light shades jute may be bleached to a pale cream color by steeping for 1 to 2 hours in bleaching powder solution (1–2 g. chlorine per liter) at 30–40°, souring and washing. Jute has affinity for all the dyes used for cotton as well as for acid and basic dyes; the choice is based mainly on cost, and cheap, bright colors are used. Direct cotton dyes are applied from a boiling liquor with the addition of common salt, and they are used largely in dyeing for the carpet trade. Acid dyes are also extensively used; the dyebath is made up with about 5% of alum or formic acid and dyeing is carried out at the boil. Bright and intense shades are obtained with basic dyes without a mordant, although the actual substantivity is small. They are applied from an acetic acid bath, dyeing being commenced at room temperature and finished at about 70°. Sulfur Blacks and Browns are used on jute with precautions for avoiding a high pH that would damage the fiber; the dye is dissolved in the minimum amount of sodium sulfide solution and dyeing carried out at the boil with the addition of salt.

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[68] White, *J. Soc. Dyers Colourists* **55,** 409 (1939); Grundy, *ibid.* **60,** 205 (1944); Boulton, *ibid.* **62,** 65, 77 (1946); Saville, *Am. Dyestuff Reptr.* **35,** 51, 58 (1946); Fidell, Royer and Millson, *ibid.* **37,** 166 (1948).

[69] Vickerstaff, *J. Soc. Dyers Colourists* **59,** 92 (1943).

[70] For a critical discussion of the application of chrome dyes to nylon, see Hadfield and Sharing, *J. Soc. Dyers Colourists* **64,** 381 (1948).

UNION DYEING

Dyeing problems are considerably increased when fabrics containing more than one fiber have to be dyed, but such union materials have become increasingly popular as a result of the development of the rayons and the synthetic fibers. Common unions are cotton and viscose, cotton and wool (the oldest union), wool and viscose, silk and viscose, wool and silk (gloria), and acetate rayon in admixture with cotton, viscose, silk, and wool. When the yarns are dyed separately and then woven into fabric, there is obviously no question of union dyeing. The dyeing problem is relatively simple when one of the fibers (usually the cotton warp) has been yarn-dyed, and is woven with an undyed weft; the warp dye must be fast to the "cross dyeing." The real complexities of union dyeing are encountered when all the fibers are woven in the grey state and the piece is then dyed. The commercial advantages of such union dyeing are that the grey goods can be stocked in bulk and piece lengths may be dyed to meet varying shade demands. The object may be to dye the piece a solid shade or in multicolor effects (commonly two colors, since the common unions are of two fibers). For solid shades on unions containing both cellulose and protein fibers, the only class of dyes that can be used are the direct cotton dyes, and few meet all the requirements. The temperature and salt addition must be carefully controlled. Cotton-viscose unions can be dyed with carefully chosen dyes of the direct, sulfur, azoic, vat, or solubilized vat class; and the essential problem is to restrain the affinity of the rayon so as to have the same depth of shade on both the fibers. Unions of cellulose acetate with cotton or viscose can be dyed a solid shade or in two colors from the same bath by using a direct cotton dye together with a dispersed dye for the acetate rayon, adding a dispersing agent if necessary to prevent the coagulation of the acetate dye. Cotton-wool and similar unions are frequently cross-dyed by dyeing the protein fiber first with an acid dye, and then dyeing the cellulose fiber with a substantive dye at a moderate temperature (50–60°).

TEXTILE PRINTING

Textile printing[71] may be defined as localized dyeing; the coloring is restricted to definite parts of the fabric forming a design or pattern. Colored patterns can be produced by weaving, but their production by a printing method is cheaper and there are many designs that would be difficult or impossible to weave. Textile printing refers to the printing of fabrics, although yarn is printed for special purposes and yarn printing machines are available; fabrics made from any fiber or mixture of fibers can be printed, but printing is mostly carried out on cotton cloth of a plain weave (calico) and to a smaller extent on wool, silk, viscose and acetate rayon.

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[71] Knecht and Fothergill, The Principles and Practice of Textile Printing, 3rd ed., Griffin, London, 1936.

Localization of color within the limits of a pattern becomes possible by the use of a "thickener," which therefore plays a vital part in printing; the function of the thickener sharply distinguishes the dyeing and printing processes. The common thickeners are starch (especially wheat and maize starch), modified starch (British gum or dextrin, prepared by roasting dry starch at 150–200° or at a lower temperature with a little nitric acid), and natural gums (e.g., gum tragacanth and gum arabic). Colloresin DK is a methylated cellulose, which is used as a thickener for special purposes; it forms a colloidal solution in cold water, which coagulates on heating or on treatment with alkali. Colloresin V is the sodium salt of cellulose carboxymethyl ether, prepared from beechwood sawdust and therefore containing lignin. Albumen and casein are used occasionally as thickeners as well as fixing agents for printing insoluble lakes and pigments, but these are now applied with the aid of synthetic resin binders. When a dye is made up with the thickener to form a printing paste, which is applied to a fabric by a suitable mechanical device, such as a block or an engraved roller, and the fabric is dried immediately, the dye is confined within the precise limits of the pattern. In the normal methods of printing, the printed and dried fabric is submitted to the action of steam (ageing). Several types of steaming apparatus are employed. In the "rapid ager" the fabric passes through a chamber in which it comes into contact with live steam at 100–103°; a variable speed drive enables the steaming time to be altered from about 2 to 10 minutes. While the cloth is guided by means of two series of rollers (one at the top and one at the bottom) in the rapid ager, the festoon ager is a recent modification in which there is less tension on the fabric; the fabric is carried on rods travelling along the top of the machine by means of endless chains, and hangs in loops. The festoon ager is especially useful for prolonged steaming. The old "cottage steamer" or "steaming cottage" is still in use for specialized styles such as (1) the dyed madder style, in which steaming after dyeing and oiling gives additional brightness; and (2) wax-batik styles after hand block printing with chrome or Alizarin type colors (e.g., Persian berry extract with chrome mordant). The cottage steamer is essentially an autoclave in which steam at pressures up to 30 pounds enters the interior beneath a false bottom and steam is also admitted to a cavity roof; when the printed pieces, wound between grey pieces ("greys") have been placed inside, the cottage is closed and steam admitted. An important modern development is the star steamer, particularly popular with block and screen printers who print vat and discharge styles, in which the cloth is wound radially (with interspacing) and inserted in a vertical cylindrical steam chamber with the steam passing upwards through it. Contact of the printed material with steam destroys the thickener membrane; the fibers swell simultaneously and the dye diffuses inside the fiber. In some printing processes, the action of steam also results in the reduction of the dye (e.g., vatting of a vat dye or the destruction of an azo dye) or oxidation of the dye or fixation of the dye as a lake. The fabric is then given one or more wet treatments for washing off the thickener and auxiliary chemicals, completing the development and fixation of the color, and improving the fastness of the print.

Prints may be produced by means of (1) blocks in which the design is in relief, and the blocks may be hand or machine operated; (2) rollers in which the design is engraved or "intaglio"; and (3) stencils and screens. Hand block, stencil, and screen printing are largely used for special effects, but the bulk of textile printing at the present time is carried out on the cylinder or roller printing machine in which cloth under tension passes through the nip between an engraved copper roller carrying the color paste and a large cast-iron cylinder padded with a woollen or rubber blanket. A series of copper rollers can be set round the iron bowl, and multicolor designs can thus be printed in one operation. In ordinary roller printing with thickened printing pastes, the roller engraving is deep in comparison with paper printing by the rotogravure process, but textiles can be printed by methods very similar to rotogravure printing on paper by using pigments finely dispersed in resin media.

The nature of the printing process, involving at least three distinct stages of printing, steaming, and aftertreatment, necessitates the use of a much larger number of acids and alkalis, oxidizing and reducing agents, solvents and auxiliary substances, than in dyeing. Of particular importance is sodium sulfoxylate-formaldehyde ($NaHSO_2$, CH_2O, $2H_2O$), made by the action of zinc dust on a mixture of formaldehyde and sodium bisulfite or hydrosulfite, and known under various commercial names (e.g., Rongalite C; Formosul; Hydraldite; Sulfoxite). This stable substance acts as a reducing agent during the ageing process.

Styles of printing. Printing processes are customarily classified into four "styles": (*a*) direct, (*b*) dyed, (*c*) discharge, and (*d*) resist.

The direct style is the simplest and most largely used. The color is applied directly in one operation, and the fixation is effected during ageing, followed if necessary by suitable aftertreatment. Fixation might only involve the coagulation of the thickening and penetration of the color into the fiber (substantive dyes); or it might involve chemical reactions such as diazonium coupling (azoic dyes), lake formation (mordant colors), reduction and oxidation (vat dyes), or hydrolysis and oxidation (Indigosols). The direct style is sometimes known also as the steam style, but the former defines the style better. In the early days of printing the styles were limited by the narrow range of dyes available, and the steam style referred especially to the fast, bright prints of the Alizarin lakes. All the classes of synthetic dyes can now be applied in the direct style, and further, steaming or ageing is also necessary for printing in the other styles. The following are two examples of the direct style. (1) Calico is printed with a paste of a vat dye, potassium carbonate, sodium sulfoxylate-formaldehyde, starch-tragacanth thickening and glycerol, prepared a few hours earlier so that partial reduction and uniform dispersion of the dye have taken place. After drying in hot air, the fabric is immediately aged for a few minutes at 102–103°, passed through a cold, very dilute solution of sodium dichromate and sulfuric acid, and soaped at the boil. (2) Silk is printed with a paste containing an acid-mordant color, glycerol, British gum thickening, chromium fluoride and ammonium oxalate, dried, steamed in the cottage for one hour, washed, soaped at 60°, washed and dried.

Dyed style. An important example is the madder style. The mordant (e.g., aluminium acetate) is first printed and fixed by drying, ageing and treating with a warm solution of trisodium phosphate or ammonium carbonate and malt (to remove the starch thickening). The mordanted fabric is then dyed with a suspension of the mordant dye (chiefly Alizarin)to which is added glue, Turkey Red oil, chalk and tannin; washed, " oiled," dried, and aged again. Soaping and a treatment with bleaching powder solution to " clear the whites " complete the long process, which is one of the oldest printing styles and still in use because of the brilliance and fastness of the prints. Multicolor prints can be obtained by printing with different metallic mordants and dyeing with a polygenetic dye such as Alizarin. Two-stage methods of printing azoic dyes, such as printing with " naphthols " and developing the printed fabric by padding with a solution of a diazonium salt, can also be included in the dyed style.

The discharge style in its simplest form consists in printing a dyed fabric with a composition which, on drying and ageing, destroys the dye in the printed pattern. Thus, if a fabric dyed an azoic red is printed with a starch-tragacanth paste containing sodium sulfoxylate-formaldehyde, zinc oxide, potassium carbonate, sodium *N*-benzylsulfanilate (" Solution Salt B," a solubilizing agent) and anthraquinone (as a reduction catalyst), followed by the usual ageing and other treatments, a white print on a red ground is produced. By incorporating a blue vat dye in the printing paste and omitting the zinc oxide, a color discharge (a blue print) on a red ground is obtained. Another way of producing a color discharge is to have a ground dyeing of two components (e.g., Diamine Sky Blue and Primuline), only one of which is dischargeable; a sodium sulfoxylate-formaldehyde discharge on this mixed dyeing gives a yellow discharge on a bluish green ground.

Resist (or reserve) style. If a water-repellant wax is printed and the fabric is then dyed cold, the dye penetrates through the cracks in the wax, and also dyes the unprinted portions, so that a fine line or veined effect on a colored ground is obtained. This is a mechanical resist which is used in Java, but much more common are chemical resists. If calico is impregnated with an alkaline solution of a "naphthol," dried, printed with a paste containing stannous chloride, dried and developed with a diazonium salt, the color will not develop in the printed portions as a result of the reducing action of the stannous chloride on the diazonium salt; a white resist under a colored ground is thus obtained. Similarly, the development of aniline black can be resisted by printing with a paste containing sodium acetate and zinc oxide which liberate volatile aniline, or with an alkaline reducing agent which prevents oxidation by acid chlorate; and the development of an Indigosol can be resisted by printing with a paste containing potassium carbonate and sodium sulfoxylate-formaldehyde so that hydrolysis and oxidation of the Indigosol cannot take place. By incorporating in the resist paste a dye which is unaffected by the reagents which are present, a colored resist under a colored ground can be produced.

Printing colors. A printing paste is made up of the soluble or insoluble dye, thickener, and the necessary reagents, agitated for some time, and then strained carefully through fine calico. The object is to produce a uniform paste completely free from grit, since many printing faults otherwise arise. To facilitate the work of the printer in the production of satisfactory printing pastes, special printing brands of insoluble dyes, particularly the vat dyes, are therefore marketed. Special printing compositions are also manufactured for the application of the azoic dyes in printing by methods unsuitable for dyeing.

Progress in printing has naturally run parallel with developments in dyes and dyeing. The chemical reactions involved are more complicated than in dyeing because of the circumscribed nature of the processes and the varied effects that may be desired. Apart from the wide range of dyes with the necessary brilliance and fastness which the printer can now utilize, his work has been facilitated by improved thickeners, mordants, developers, catalysts, and auxiliary agents.

PIGMENT PRINTING

Pigment processes of calico printing, comprising the use of pastes containing a synthetic resin, water-insoluble dyes, and an organic solvent, are coming into vogue; these have been developed from the old pigment printing process with albumen or casein as fixing agent. The Aridyes

(Interchemical Corporation) were the first printing pastes of the type to be marketed, and the patent literature[72] gives evidence of the current interest in pigment printing. The Aridyes are three-phase emulsions with an outer continuous water-immiscible lacquer phase and an inner aqueous phase, the binding resin being incorporated as a solution in a suitable solvent. The resin is generally an alkyd, and the coloring matters are of the anthraquinonoid vat, azoic, and phthalocyanine class. After printing, drying, and curing the fabric at 120–150° for a few minutes, the binding action of the resin is adequate for good fastness to washing, but the fastness of the prints to rubbing is only moderate. Infrared radiation may be used for curing the pigmented resins. If the limitations of the present range of pigment emulsions can be removed, the method will undoubtedly prove to be a great advance in calico printing.[73] The utility of the Aridye and other types of pigment emulsions for piece dyeing is being investigated, especially in the United States.[73a] Poor fastness to rubbing is one of several problems, but with the developments that are taking place on resins and plasticizers, it is not unlikely that the defects will be remedied. The advantages of pigment-resin emulsions in dyeing are their suitability for continuous processing and bulk production, the uniformity of the shades, and their fastness to light and wet treatments.

"Orema" dyes, described as a new class of dyes for textile printing, are very finely divided pigments made into stable pastes, which give clear bright prints by fixation at 100–120°. If carragheen moss is added, slop padding methods may be used.[74] The Orema dyes have been withdrawn from the market, apparently because of the inferior fastness of the prints.

AUXILIARY AGENTS USED IN DYEING

Besides inorganic compounds such as sodium hydrosulfite, nitrite, and chloride, organic products of varying complexity are employed in dyeing processes. These belong to the general class of textile auxiliary agents,[75, 76, 77] possessing one or more of such properties as wetting, detergency, emulsifying power, and protective colloidal action. Among the purposes for which they are used in dyeing are the dispersion of dyes, wetting out of fibers, and level dyeing. The oldest and cheapest dyeing assistants are soaps, Turkey Red oil, Monopole oils, and other products obtained by the action of sulfuric acid on castor oil and similar oils containing unsaturated and hydroxylated acid components. Substances with greater wetting power and stability were then prepared by the treatment of methyl and ethyl oleate and ricinoleate with sulfuric acid or oleum. The wetting agents now available commercially are too numerous to mention.[76] Chemically the great majority are anion-active colloidal electrolytes belonging to a general type, being sodium salts of sulfonic acids and of acid sulfuric esters ($R\text{-}SO_3Na$ and $R\text{-}O\text{-}SO_3Na$) derived for instance from the higher alcohols (e.g., lauryl and cetyl alcohol, 2-ethylhexanol), alkylbenzenes, and alkylnaphthalenes. Nonionic compounds, such as polyethylene glycols and their derivatives which have solvent and wetting properties, and cation-active substances such as quaternary ammonium salts carrying a heavy alkyl group, have their uses. Recent reports on the German dyestuff industry disclose the methods of preparation of many textile auxiliary agents.[78]

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[72] See for example USP 2,308,763; 2,322,837; 2,323,871; 2,338,252; 2,421,000; 2,474,909; BP 539,737; 543,860; 547,059; 555,289; 560,049; 561,641; 573,558; 602,886.

[73] For discussions of the advantages and disadvantages of pigment printing, see *J. Soc. Dyers Colourists* **61,** 38, 85 (1945); *Dyer*, 353 (1947); Silverman, *Am. Dyestuff Reptr.* **37,** 44 (1948); Hasse, *Melliand Textilber.* **24,** 277 (1943); Cassell, *Am. Dyestuff Reptr.* **28,** 341 (1939); IG work on pigment printing is described in *BIOS* **1088.**

[73a] E.g., Kuhn and Bodenschatz, USP 2,488,544; Interchem. Corp., BP 631,882.

[74] Krahenbuhl, *Melliand Textilber.* **24,** 315 (1943).

[75] Chwala, Textilhilfsmittel, Springer, Vienna, 1939. (Photo-Lithoprint Reproduction, Edwards, Ann Arbor).

[76] Venkataraman *et al.*, *J. Soc. Dyers Colourists* **53,** 91 (1937), *et sequa.*

[77] Schwartz and Perry, Surface Active Agents, Interscience, New York, 1949.

STRIPPING OF DYED AND PRINTED MATERIALS

In view of the variations in the dyeing properties of textile materials from batch to batch and the general difficulties inherent in dyeing and printing processes, it is inevitable that unlevel shades, as well as wrong tones and depths of shade, should be occasionally produced. The only remedies then are to overdye the material in a dark drab shade of grey, brown, or black; or to strip the original print or dyeing, and redye. In dealing with garments and fabrics such as Indian saries, dyed or printed, stripping and redyeing are frequently practised. The stripping or removal of dyes from dyed and printed materials is therefore an essential part of the technology of dyeing and printing. Methods of stripping consist mainly in reductive or oxidative decomposition of the dye, but when this is not possible without damage to the fiber, the dye may be dissolved in the presence of a powerful retarding agent for preventing reabsorption by the fiber. Azo dyes are removed by reduction, by alkali and hydrosulfite for cellulose fibers, and formaldehyde-sulfoxylate in presence of acetic acid for wool and silk.[79] Zinc Formosul (Decroline, IG) is useful as a stripping agent. In stripping azoic dyes, a useful auxiliary agent is

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[78] *BIOS* **239, 259, 418, 421, 518, 711, 1151, 1768, 1773**; Misc. Repts. **11, 12, 89**; *FIAT* **1013**; *CIOS* Item 22, File XXX–10; XXVI–2; Item 8, 22, 24, 30, File XXV–26.

[79] Starkie, *J. Soc. Dyers Colourists* **63**, 340 (1947).

Lissolamine A (ICI), a quaternary ammonium salt (of the type trimethylcetylammonium bromide) containing a long paraffin chain,[80] which maintains the azoic dye in a dispersed state in which it can be readily attacked by the reducing agent. A mild bleach usually follows the reduction. Many acid dyes on wool may be stripped by boiling with a solution of Glauber's salt and a little ammonia. It is difficult to strip vat dyes from cotton completely, but the shade may be reduced sufficiently to enable redyeing by treating the material with a solution of caustic soda and hydrosulfite at or near the boil with the addition of Lissolamine V (ICI) or a protective colloid auch as Peregal O (IG).[81] The stripping of vat dyeings by means of formamidinesulfinic acid (a product of the action of hydrogen peroxide on thiourea) and caustic soda solution has been suggested.[82] A combination dye-stripper has been described in which an active oxidizing agent (e.g., sodium perborate and a manganese salt) and a latent reducing agent (e.g., sodium sulfoxylate-formaldehyde coated with a substance insoluble at low temperature) are used together.[83] Dispersed dyes on acetate rayon can be stripped by treatment with soap solution at about 80° in presence of activated carbon; or by solvents such as a mixture of methylene chloride (which acts as a swelling agent) and petrol.[84]

FASTNESS TESTS AND STANDARDS

The fastness or stability of a dye is not an absolute property. The agency towards which the fastness is being considered has to be specified; and the fastness to a given agency (e.g., light) depends further on the medium (textile, paint, lacquer, plastic) to which the dye has been applied. Considering the fastness in relation to textiles, it is well known that the same dye may exhibit considerable differences in fastness properties according to the nature of the fiber which is dyed, the weave and surface characteristics of the fabric, the depth of the shade, and other factors. When we speak therefore of the fastness of a dye, the reference is to a dyed shade and not to the dye itself. However, it is important from the points of view of both dye makers and dye users that there must be a standardization of fastness tests for the assignment of grades of fastness to a given dye. A fastness committee (Echtheitskommission) was appointed in Germany in 1911, and the report, published in 1914, represented the first systematic study of fastness tests and standards. Methods were described for preparing the standards, carrying out the tests, and assigning numbers to indicate the degrees of fastness. Extensive investigations have since been undertaken by the leading dye manufacturers, the Society of Dyers and Colourists (SDC)[85] in England and the American Association of Textile Chemists and Colorists (AATCC);[86] and a Fastness Committee of the SDC appointed in 1944, with which the AATCC is collaborating, is due shortly to make a new report.[87] Fastness to light is graded from 1 to 8, and all other fastness properties from 1 to 4 or 5, the fastness increasing with increasing numbers; by this procedure, higher grades can be assigned if faster dyes are discovered in the future. For greater accuracy in the grades assigned, the fiber, the strength of the dyeing, and the conditions of dyeing are specified. Since the alterations in depth and tone of a dyeing are only examined visually, an absolute assignment of grades is not possible, and it is necessary to make a comparison with a set of standard dyeings on which the same tests are simultaneously carried out.

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[80] Evans, Lawrie, and ICI, BP 400,239; 422,466; 422,556; Rowe and Owen, *J. Soc. Dyers Colourists* **52,** 205 (1936).

[81] See also Geigy, SP 217,128–9.

[82] du Pont, USP 2,206,535.

[83] Block, USP 2,077,983.

[84] Moncrieff, BP 513,077.

Fastness properties relate to two classes of agencies likely to affect a given dyeing. One includes further processes which the dyed material has to undergo, such as kierboiling, mercerization, bleaching and finishing treatments for cotton, and milling, potting, degumming, stoving, carbonizing, and decatizing for wool and silk. The other represents the fastness properties with which the user of the dyed and marketed material is concerned—fastness to washing and commercial laundering, sea-water, light, perspiration, rubbing or crocking, and hot ironing. A few of the procedures laid down by the AATCC as the official or tentative standard methods of testing for these fastness properties are outlined.

Fastness to light. This test is applicable to dyed or printed textile fibers of all kinds. The dyed specimens, side by side with the standard dyeings, are exposed to (*a*) sunlight in a sun exposure cabinet covered with window glass and open at the sides to allow free access of air, or (*b*) artificial light in a Fade-O-Meter, a carbon arc lamp in which the specimens rotate about the arc, the surrounding air being humidified (R.H. less than 50%) and maintained at a constant temperature (46° or less).[87a] Sunlight exposure tests are on the whole the most reliable. Each specimen is placed between opaque covers, shielding it from light except for an area about $1\frac{5}{8}$ by 2 in. The specimens are exposed until slight fading is noticed. Fading denotes any change in color, and not merely a weakening of the shade. Table II gives the number of hours of exposure in which the fastness standard can be gauged in comparison with the standard dyeings; for a satisfactory comparison, a second set of specimen and standard is exposed for double the number of hours in the table.

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[85] Reports of the Society of Dyers and Colourists on the work of its Fastness Committee in fixing standards for light, perspiration and washing, 1934.

[86] See Year Book 1949.

[87] *J. Soc. Dyers Colourists* **64**, 133 (1948).

[87a] See also *BIOS* **1818**.

TABLE II

Standard	1	2	3	4	5	6	7	8
Sun test hours . . .	1.5	3	6	12	24	48	96	192
Fade-O-Meter test hours .		2.5	5	10	20	40	80	160

In stating the fastness to light of a dyestuff as judged by the fastness of a dyeing made from it, it is especially important to state the strength of the dyeing, since weaker shades in general fade more rapidly.

Fastness to commercial laundering and to domestic washing (cotton and linen). The test is carried out in a standard apparatus, the Launder-O-Meter, and covers the range of fastness from neutral soap at 105° F. to severe washing at 182° F. with alkaline soap and a bleaching agent. The Launder-O-Meter consists of a copper waterbath, maintained at the desired temperature, in which rotates at a standard speed of 42 r.p.m. a brass and aluminium rotor carrying 20 standard pint jars of glass. The test specimen is made up by attaching to the dyed or printed fabric (2 × 4 in.; or dyed yarn knit to the same size) a 2 inch square of multifiber test cloth or white calico. Each specimen is placed in a glass jar containing 100 cc. of one of the solutions mentioned in Table III, together with ten $\frac{1}{4}$ inch stainless steel balls; the jar is closed and the machine run at the temperature and for the time specified in Table III. The specimen is now removed, rinsed successively with two lots of 100 cc. water at 105° F., 100 cc. of a 0.05% solution of acetic acid at 80° F., and 100 cc. water at 80° F., hydro-extracted, and dried by pressing with an iron (at 275–300° F.). The fastness is then graded in accordance with the maximum number of the test in which the specimen shows no appreciable change in color and no appreciable staining of the attached test cloth.

TABLE III

Test No.	*Temp. °F.*	*Soap conc.%*	*Sodium carbonate conc.%*	*Available chlorine %*	*Time mins.*
1	105	0.5	None	None	30
2	120	0.5	None	None	30
3	160	0.5	0.2	None	45
4	182	0.5	0.2	0.01	45

Standards for comparison are made by dyeing Diamine Fast Blue FFB (prototype CI 71), 2% shade (grade I); Primuline conc. (CI 812), 4% shade, diazotized and developed with β-naphthol (grade II); Vat Blue 2BD (CI 1184), 2% shade of 100% powder (grade III); and Vat Violet BN (CI 1163), $2\frac{1}{2}$% shade of 100% powder (grade IV).

Fastness to perspiration. The test is applicable to all fibers. Since human perspiration can be acid or alkaline, both acid and alkaline solutions have to be used for the test. Each solution contains 10 g. sodium chloride and 1 g. disodium hydrogen phosphate per liter; the acid solution contains in addition 1 g. lactic acid, and the alkaline solution 4 g. ammonium carbonate. The tests are carried out in glass tubes 75 × 15 mm. or 120 × 22 mm., which are placed in a drying oven at 100° F. ± 2°, or in a desiccator containing 70% sulfuric acid at room temperature. The test specimen is made up by taking a piece of the dyed or printed fabric (or knitted yarn) about 2 inches wide and of such length that, when rolled with the multifiber test cloth of similar size, the roll just fits the bore of the tubes. The four tests corresponding to grades 1 to 4 differ only in the time of treatment : 40 minutes, 2, 6, and 18 hours. A test specimen and multifiber test cloth are thoroughly wetted with the acid solution, so that the weight of the two is about trebled. The two pieces are then rolled together with the test specimen on the inside, inserted in a glass tube, so that one-third of the roll projects outside, and the tube standing on end in a rack is then placed in the oven or desiccator. A similar test is performed with the alkaline solution. On removal, the specimens are dried without rinsing, and the fastness graded according to the maximum number of the test in which the staining of the multifiber test cloth is no greater than Munsell Neutral Value Scale No. 8 and there is no appreciable migration and change in color.

NONTEXTILE USES OF DYES

Apart from their application to textiles, dyestuffs are used for many purposes, divisible into two classes. The first is the coloration of various materials other than textiles, such as paper, leather, oils, soap, plastics, paints, varnishes, lacquers, printing inks, foods, drugs, and cosmetics. Dyeing anodized aluminium is a recent application. Uses of dyes as indicators, staining agents in bacteriological and histological work, and sensitizers of films and plates for photography, are also based on the tinctorial or light-absorption characteristics of dyes. The second includes noncoloring purposes, depending on the incidental properties of dyes, such as antibacterial and chemotherapeutic activity.

Pigment-using industries.[88, 89] It is customary to distinguish between dyes and organic pigments on the basis of solubility in water. Dyes are either soluble in water; or can be solubilized by simple chemical

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[88] Mattiello, Protective and Decorative Coatings, II, Wiley, New York, 1942.

[89] Pratt, The Chemistry and Physics of Organic Pigments, Wiley, New York, 1947.

treatment (such as reduction with sodium sulfide or hydrosulfite), reversible in a simple manner to regenerate the parent dyes. Pigments are insoluble in water, and are applied for coloring purposes by a process of dispersion. Pigments for paints should also be insoluble in oils, since bleeding into oils (e.g., from one coat of paint into the next) will otherwise occur; and they should have opacity or hiding power. Dyes of the second type mentioned above (e.g., vat dyes) function as pigments if they are not solubilized, but dispersed in a suitable medium and then used for coloration, whether the application is to a textile or other material. A soluble dye is converted into a pigment when precipitated as a lake (e.g., the barium salt of a sulfonic acid or the phosphotungstic salt of a basic dye precipitated on a substrate);[90] and conversely a pigment, such as copper phthalocyanine, can be converted into a dye by the introduction of sulfonic groups. It follows therefore that the chemistry of dyes includes the organic pigments.

The use of organic dyes and pigments for protective and decorative coatings and for coloring such materials as plastics and printing inks is next in commercial importance only to the use of dyes for dyeing and printing textiles. The largely used organic pigments are (1) lakes prepared from basic dyes of the triphenylmethane and other classes by precipitation with tannin-tartar emetic, rosin or fatty acids, or phosphotungstic, phosphomolybdic and phosphomolybdotungstic acids; (2) lakes prepared from acid dyes and alkaline earth or heavy metal salts; (3) calcium-aluminium lakes of Alizarin and its derivatives; (4) azoics; (5) vat dyes, especially the anthraquinonoids; and (6) phthalocyanines.

As in the case of dyes for textiles, fastness tests and standards for pigments have to cover both the processing requirements and the end use requirements. Thus a pigment for coloring a plastic must withstand the temperature at which it is cured or molded and the action of the reagents (e.g., formaldehyde and benzoyl peroxide) that are involved; and it must also be resistant to hot water, acids, alkalis, and other agencies according as the final articles are containers, spectacle frames, electrical equipment, etc. An important characteristic of a pigment, which determines its tinctorial value, is the fineness of the dispersion. The physical properties of a pigment depend on the conditions of precipitation, the dispersing agents employed, and the methods of grinding, mixing, and drying, which have to be carefully studied and controlled.[90a] A notable advance in the use of pigments and lakes for printing inks and similar products is to work an aqueous paste of the pigment in its original state from precipitation (i.e., without drying) in a Baker-Perkins type of mixer jacketed for steam-heating, together with a vehicle (e.g., linseed oil) and a surface-active compound. The pigment is transferred to the oil, and the water separates as a layer which can be decanted off. This process of "flushing" a pigment eliminates the need for drying it and achieves a fine dispersion in the desired vehicle. The last traces of moisture may be removed by heating under reduced pressure.

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[90] A distinction is made between toners which are the pure salts of dyes, and lakes, which are precipitated on substrates or fillers. Thus the sodium or calcium salt of an azo dye is a sodium or calcium toner. A lake, the word being derived from the dye of the lac insect, has been defined by the ASTM as "A special type of pigment consisting essentially of an organic soluble coloring matter combined more or less definitely with an inorganic base or carrier. It is characterized generally by a bright color and a more or less pronounced translucency when made into an oil paint." See also Blumenthal, *Am. Dyestuff Reptr.* **35,** 529 (1946).

Oil- and wax-soluble dyes (e.g., Indulines and Nigrosines) are useful in the manufacture of shoe and furniture polishes, carbon papers, crayons, candles, sealing wax, lubricating oils, and ink for ball-point pens.[91]

Colored smokes. Volatile organic pigments are employed in war time for the production of colored smokes for signals. A mixture of the pigment, potassium chlorate, and sugar is ignited to produce the smoke, and stability at high temperature is therefore essential, so that only a few pigments possess the necessary properties of color, volatility, and thermal stability. Examples of such smoke colors are 1-amino-4-hydroxyanthraquinone (wine red), 1,2,4-trihydroxyanthraquinone (brown), 1,5- and 1,8-bis-*m*-toluidinoanthraquinone (violet), and 2-bromo-1-amino-4-toluidinoanthraquinone (blue).

Camouflage colors. With the object of rendering targets undetectable by infrared photography, dispersions of the phthalocyanines and of Pigment Green (iron complex of 1-nitroso-2-naphthol) have been used.[92]

Photography. The cyanine dyes used as sensitizers in photography are treated in Chapter XXXVIII; and dyes are used also for the prevention of halos, hand coloring, and retouching of photographic prints. Selected textile dyes (e.g., among the acid colors), as well as dyes specially made to meet the requirements, are employed. Color formers in photography are discussed in Chapter XXXIX.

Fluorescent dyes are used for dyeing and printing theatrical fabrics, carpets in cinemas and other purposes, for instance in connection with A.R.P. measures, in which luminescence in the dark is desired. Luminescent dyes, activated by ultraviolet light and with the important property of having no afterglow, were used during the war for night-marking of streets and direction signs, and on railroad beds for detecting sabotage.[92] The "Lumogen" colors used by the Germans belonged to varied chemical types. The intense green fluorescence of Fluorescein has long been used for such purposes as the detection of leaks in drains and of the passage of water through subterranean channels. During the war airmen were provided with a package of Fluorescein which they released if forced down into the sea, so that rescuers might be guided by the green patch, which could be seen at a great distance.[91]

[90a] Stead, *J. Oil & Colour Chemists' Assoc.* **30,** 337 (1947).

[91] For an account of miscellaneous applications of dyes, see Gill, *J. Soc. Dyers Colourists* **64,** 213 (1948).

[92] *CIOS* XXVII–84.

The efficiency of solar evaporation of sea water and other natural salt waters for the manufacture of common salt and other salts can be increased by the addition of a dye for increasing the amount of absorbed radiation.[93] Solivap Green (ICI), which has very good light fastness and infrared absorption, has been found to be particularly effective.[93a]

Indicators and analytical reagents. Several dyes are useful as pH indicators (e.g., phenolphthalein and other phthalein dyes, Methyl Orange, Methyl Red, Brilliant Yellow, Congo Red); oxidation-reduction indicators (e.g., Methylene Blue, Indigocarmine, Xylene Cyanol FF); adsorption indicators in volumetric analysis (e.g., Dichlorofluorescein, Eosine, and Rose Bengal in the titration of halides with silver nitrate) and indicators for the presence of soap micelles in aqueous systems.[94] Certain dyes, which change color at specific temperatures, have been used for observing temperature variations in different part of machinery. Many dyes are useful as analytical reagents[95] for the detection and determination of metals. Examples are Naphthol Yellow S (Co, Hg, K, Rb); Orange IV (Zn, Mg); Clayton Yellow (Mg); Benzo Fast Yellow 5GL (Cr, Cu, Fe, Ni); Direct Green B (Cu); Eriochrome Blue Black B (Co); Acid Alizarine Yellow RC (Cr); Chromotrope 2B (Ge, B); Diamond Black F (several metals); Safranine (Sb, Hg, Ag); Gallocyanine (several metals); Methylene Blue (several metals, as well as negative radicals); Rhodamine B (several metals); Naphthazarin (Al, Be, Mg); Alizarin and its derivatives (Al and other metals). Many dyestuff intermediates are also useful analytical reagents.[96]

Food colors. It has long been recognized that food, in addition to fulfilling the requirements of nutrition, taste, and odor, may be made more acceptable by coloration. Coloring foodstuffs, such as sweets, confectionery, sausage meat, oils, butter and margarine, as well as beverages, has therefore been common practice. Natural coloring matters (e.g., annatto, chlorophyll, cochineal, saffron, and turmeric) were originally employed and are still in use; but the synthetic dyes, with the advantages they possess of variety of shades, cheapness, and ease of handling, are now extensively used. Synthetic dyes cannot be used indiscriminately for coloring food, since many dyes are toxic; and food colors have to be manufactured in a high state of purity and free from harmful constituents such as arsenic and lead. In the United States, only the "certified colors" listed later can be used.[97] For all food colors the maximum limit for arsenic as As_2O_3 is 0.00014%, and for lead 0.001%. Only a trace of other heavy metals, precipitable as sulfides, is permitted, and no barium lakes are permitted. A food color may be added only in an amount not exceeding 2 grains per pound. There are in addition 69 colors certified as usable in drugs and cosmetics only, and 29 in externally applied drugs and cosmetics, with the proviso that no coal-tar dye whatsoever can be used in a product applied to the area of the eye. The list of certified colors is of value also in choosing dyes for coloring dolls and toys, used by children who are likely to put them in their mouths, and articles which come into contact with the human skin. Manufacturers have to submit samples so that the Food and Drug Administration of the Federal Security Agency may determine if the color conforms to the specifications set down under the Federal Food, Drug and Cosmetic Act.[98] These 18 certified colors are: Naphthol Yellow S (CI 10); Naphthol Yellow S, potassium salt (CI 10); Yellow AB (CI 22); Yellow OB (CI 61); Tartrazine (CI 640); Sunset Yellow FCF; Orange I (CI 150); Orange SS; Ponceau 3R (CI 80); Amaranth (CI 184); Erythrosine (CI 773); Ponceau SX; Oil Red XO; Brilliant Blue FCF; Indigo Carmine (CI 1180); Guinea Green B (CI 666); Light Green SF Yellowish (CI 670); and Fast Green FCF.

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[91] See p. 300.

[93] Halperin, *Chem. Eng.* **54,** June, p. 94 (1947).

[93a] *Dyer* **103,** 759 (1950).

[94] Corrin and Harkins, *JACS* **69,** 679 (1947); see also Arkin and Singleterry *JACS,* **70,** 3965 (1948).

[95] Welcher, Organic Analytical Reagents, IV, Van Nostrand, New York, 1948.

[96] *Ibid.,* I, II, III.

In Great Britain dyes are not certified as food colors, but certain dyes are prohibited, and among these are picric acid (CI 7), Victoria Yellow (CI 8), Manchester Yellow (CI 9), Aurantia (CI 12) and Aurine (CI 724). Compounds of arsenic, antimony, cadmium, chromium, copper, mercury, lead, and zinc are prohibited. The American procedure of specifying colors which have definitely been found to be safe after careful pharmacological and toxicological tests is much to be preferred. Indeed it is a matter for consideration whether the safest and most rational practice will not be to use as food colors the natural coloring matters present in edible plant materials.[99]

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[97] For their properties and specifications, see Jacobs, Synthetic Food Adjuncts, Van Nostrand, New York, 1947.

[98] Calvery, *Am. J. Pharm.* **114**, 324 (1942).

[99] Cf. Cox, *Chemistry and Industry* 30 (**1944**); see also *Nature* **149**, 537 (1942); Desai and Venkataraman, *J. Indian Chem. Soc., Ind. & News Ed.* **5**, 165 (1942).

Medicinal dyes. Ehrlich's discovery of the selective staining of nerve cells by Methylene Blue, and later observations that certain dyes stained and paralysed specific microorganisms, led to the use of dyes as antibacterial and chemotherapeutic agents. While dyes have continued to be very valuable for staining and other purposes in pathological and medical research, their use in chemotherapy has diminished considerably with the discovery of more effective substances such as the sulfanilamides, penicillin, and streptomycin. Mercurochrome and acridine derivatives such as Acriflavine are still largely used, and among the dyes which have a limited application as bactericides are the triphenylmethane dyes, Malachite Green, Brilliant Green, Methyl Violet, Crystal Violet, and Gentian Violet. Aminoazotoluene and its mono- and diacetyl derivatives (Azodermin; Dimazon; Pellidol) and Biebrich Scarlet are used for stimulating the growth of skin over wounds. Pyridium (3-phenylazo-2,6-diaminopyridine monohydrochloride) is a genitourinary antiseptic. Various other azo dyes have been used in the past as medicinals, and examples are Trypan Red and Trypan Blue for sleeping sickness, Prontosil (2,4-diaminoazobenzene-4′-sulfonamide monohydrochloride, the first sulfanilamide to be used in therapy), and Neoprontosil (the azo dye from diazotized sulfanilamide and 2-acetamido-8-naphthol-3,6-disulfonic acid).

CHAPTER VII

COLOR AND ITS MEASUREMENT

If light emitted by a terrestrial or celestial body is viewed through a spectroscope, it is observed that, depending on the nature of the radiating body, a continuous colored band or discrete regions of color are produced as a result of the dispersion of the complex light by the prism in the spectroscope. Thus among terrestrial sources a coal fire shows a continuous red band fading into yellow; candle light, gas light, and electric light show spectra extending further into the green, blue, and violet. This is the visible spectrum, which covers the well-known " vibgyor " range of rainbow colors. Discharge lamps on the other hand, such as those containing certain gases and metallic vapors, give lines and bands in the visible range which are not continuous. Beyond the red end on the one side and the violet on the other there lie the infrared and the ultraviolet regions of radiation, which are not perceived by the human eye. In the consideration of color attention is usually restricted to the visible radiations.[1]

The classical theory of light identifies both the visible and invisible radiations with electromagnetic waves of definite wave lengths. The long waves ranging in length from a thousand meters and more down to a few centimeters are the radio waves. The range between 1 cm. and 0.001mm. for practical purposes comprises the heat and infrared radiations. For the consideration of still smaller wave lengths it is convenient to use a smaller unit, the micron (μ) which is 0.001 mm. The near infrared region of the spectrum just outside the visible red end is then covered by the range 1.00 to 0.80 μ. From here on towards shorter wave lengths, we pass through the complete color range: red, orange, yellow, green, blue, and violet, approximately at the wave lengths 0.65 μ, 0.60 μ, 0.58 μ, 0.52 μ, 0.45 μ, and 0.40 μ, respectively. In order to avoid fractional values, the units of measurement employed for the relatively short wave lengths are either 0.001 μ ($\mu\mu$ or mμ), or 0.0001 μ (A., the Angström unit). Thus 1 mμ =

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[1] For a bibliography of the literature on color perception and its relation to chemical structure, see Godlove, *Textile Research J.*, **17**, 185 (1947). For further accounts of various aspects of color, see Hardy, Handbook of Colorimetry, M.I.T. Cambridge, Mass, 1936; Murray and Spencer, Color in Theory and Practice, Chapman and Hall, London, 1939; Wright, The Measurement of Color, Adam Hilger, London, 1944; Evans, An introduction to Color, Wiley, New York, 1948; Report on Color Terminology, The Physical Society, 1948.

10^{-6} mm. = 10A. The shorter wave range below the violet consists of the ultraviolet, soft X-rays, hard X-rays, γ-rays, and cosmic rays, the last named radiations having extremely small wave lengths of the order of 0.01A.

EMISSION AND ABSORPTION OF LIGHT

The continuous spectrum shown by a luminous object is not uniform in its intensity over the whole range. If the radiation energy is measured by suitable instruments it is found that according to the temperature attained by the body there is a maximum in the energy output, which is in the 2.0 to 1.0 μ region of the infrared spectrum for most of the illuminants below 3,000°. As the temperature of the object rises, the radiation energy increases greatly, while the maximum shifts from the infrared to the visible spectrum. The relationship between the energy radiated at each wave length of light and the temperature of the radiating body (black body) is given by Planck's law. The color of a body at high temperatures is an indication of its temperature (color temperature). The temperatures of many celestial bodies, including the sun which has a surface temperature of 5,000° with its energy maximum in the yellow region of the spectrum, have thus been estimated. Certain stars (white dwarfs) have an estimated surface temperature of 40,000°, their color appearing as bluish white. A cavity in a platinum block heated electrically to various temperatures gives a source of light radiation which closely imitates the ideal black body of Planck.

Certain other light sources emit radiations in isolated regions of the spectrum. Discharge tubes containing gases and vapors at very low pressure are examples; excited electrically, they emit lines and bands generally in the near infrared, the visible, and the near ultraviolet regions of the spectrum. In contrast with the thermally excited molecules of the incandescent material of the Planck radiator, the electronic excitations in discharge tubes raise the energy of atoms and molecules in the gaseous state. After an active period of about 10^{-7} to 10^{-8} seconds, they fall to lower energy states, emitting radiations which correspond to the energy difference between the higher and the lower states. This conception, which is due to Bohr, is expressed by the relationship: $E_2 - E_1 = h\nu = hc/\lambda$; where E_2 and E_1 represent the energy contents of the atom or molecule in the higher and in the lower states, h the Planck constant, ν the frequency of radiation corresponding to the emission wave length λ, and c the velocity of light; $h\nu$ is the quantum of radiation.

Sodium light is mostly confined to the yellow radiations 5,889 and 5,896A.; for mercury the emission wave lengths are in the visible spectrum, 5,769-5,790A. (yellow), 5,461A. (green), 4,358–4,339A. (blue), and 4,078–4,047A. (violet). In another familiar spectacle, neon display signs, neon gas under excitation emits a large number of lines in the red part of the spectrum. Under similar conditions nitrogen, carbon monoxide, and other gases, as well as many vapors, emit bands of light in detached regions arranged in some systematic order through a range of the spectrum; these are instances of band spectra where the emitters are molecules such as N_2 and CO, as distinguished from the line spectra of atoms such as Na and Hg. The multicolored auroral displays of the polar regions are due to the nitrogen molecules of the upper atmosphere being excited by electrically charged particles shot from the sun during solar magnetic storms which occur during periods of sun spot activity. Tails of comets carry excited ionized molecules ($\overset{+}{CO}$), detected by their characteristic band spectra. Emission bands due to the diatomic molecules CH, C_2, OH, CN, NH, etc., are present in the flame spectra of burning gases and vapors.

If a thermally excited luminous body of the Planck type at a high temperature is surrounded by comparatively cooler gases, the atoms and molecules absorb their own characteristic radiations from the continuous spectrum of the hotter body, and the absorbed radiations appear as dark lines and bands superimposed on the continuous radiations. The Fraunhofer lines in the solar spectrum are due to elements in the gaseous state enveloping the hot photosphere of the sun emitting continuous radiations. There are also molecular absorption bands due to diatomic molecules such as OH, C_2, CH, CN and TiO in the spectra of the sun and stars in various stages of evolution. The planet Venus in the reflected sunlight spectrum shows the bands of carbon dioxide molecules, whereas the major planets Jupiter, Saturn, Uranus, and Neptune give evidence of the presence of ammonia and methane in their atmospheres through their respective absorption spectra. In such cases the original color of the thermally radiating body is modified by its surroundings, which partially absorb the continuous radiations in certain regions of the spectrum.

Both absorption and emission spectra have the same energy relations, with the difference that atoms and molecules absorb light in their transition to a higher state of energy, and they emit light in the process of transition to a lower energy level.

STANDARD LIGHT SOURCES

The color of an object observed in white light produces a color sensation which will be different if the object is observed in other light. An object having a red color in ordinary white light may appear dark brown or black in mercury light, and a blue object also brown or black in the light from a sodium lamp. It is therefore necessary to specify the exact nature of the light source when the color quality of an object is to be judged.

A source giving white light is naturally the most suitable, since color valuations are generally made in the light of a "white" source like the incandescent electric lamp or sunlight or daylight. Further, the incident light should contain the full range of the spectrum colors in the right proportion in order to bring out clearly the color selectivity of the object viewed. Light sources excited electronically are unsuitable as standards, although the modern tubular fluorescent lamp, in which an inner source of ultraviolet light excites linings of the tube made up from a number of fluorescent powders so as to give an integrated daylight effect, approximates a source of white light.

The ultimate standard has to be sunlight or daylight, but in view of its variations at different places and times secondary standards giving an energy distribution of all the colors in the required proportions have to be set up. The International Commission on Illumination (1931) has prescribed three illumination standards called the A, B, and C sources, which have their energies distributed in the visible region of the spectrum corresponding to those of Planck's black body radiations at color temperatures of 2,848, 4,800, and 6,500°K. The A source is the ordinary gasfilled tungsten filament

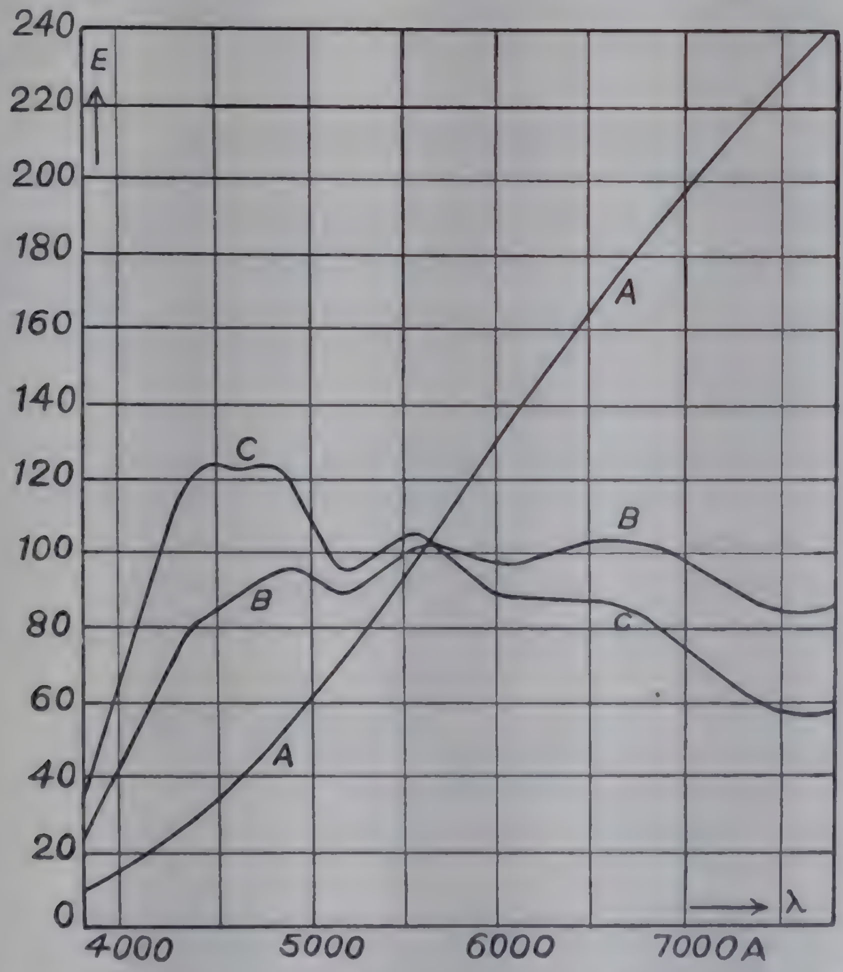

Fig. 1. Relative spectral distributions of A, B, C sources (ICI).

lamp with the temperature of the filament maintained at 2,848° by suitable control of the current consumed. It can be converted into the B (sunlight) or the C (daylight) source by interposing in its light path standard colored solutions made up from copper sulfate, cobalt ammonium sulfate, sulfuric acid, pyridine, mannite, and water, the concentrations varying according to the color requirements for the B or the C standard. With the filters for the B source the light transmitted is white, corresponding to average noon sunlight in its color and energy distribution. The light transmitted through the filter for the C source gives the daylight color, which is richer in the blue components. More convenient glass filters may replace the solution filters. However, their light transmission characteristics must be carefully checked. An incandescent filament enclosed in blue glass gives the "daylight" lamps of commerce. The B or C source is adopted in color work, A being "too yellow" on account of the greater proportion of red and yellow radiations in it as compared with sunlight and daylight, which are relatively richer in green and blue radiations. The relative spectral energy distribution curves for these three sources are shown in Fig. 1.

SELECTIVE ABSORPTION OF LIGHT

An object observed in ordinary white light appears colored if it can reflect (or transmit in the case of transparent objects) only some of the components of the incident light, which consists of all the colors in the spectrum. Light is selectively absorbed, and the object assumes the color of the unabsorbed radiations, which are reflected back. The absorbed and the unabsorbed radiations of white light are therefore complementary in character. If a spectroscopic examination is made of the light reflected by a colored body when illuminated by a source of white light, it is observed that some of the colors of the complete spectrum are missing. In the light reflected by a red object (see Fig. 2) the blue-green color is missing. Red and blue-green are therefore complementary colors. Table I gives a series

TABLE I

WAVE LENGTH OF ABSORPTION AND VISIBLE COLOR

Light absorbed		
Wave length, A.	*Corresponding color*	*Color observed*
4000–4300	Violet	Greenish yellow
4300–4900	Blue	Yellow to orange
4900–5100	Blue-green	Red
5100–5300	Green	Purple
5300–5600	Yellow-green	Violet
5600–5900	Yellow	Blue
5900–6100	Orange	Greenish-blue
6100–7300	Red	Blue-green

of wave length regions, together with the color absorbed and the observed or complementary color. These designations of color are approximate and subjective. Further, absorption is often in more than one region of the visible spectrum and the color observed also depends on the intensity of absorption.

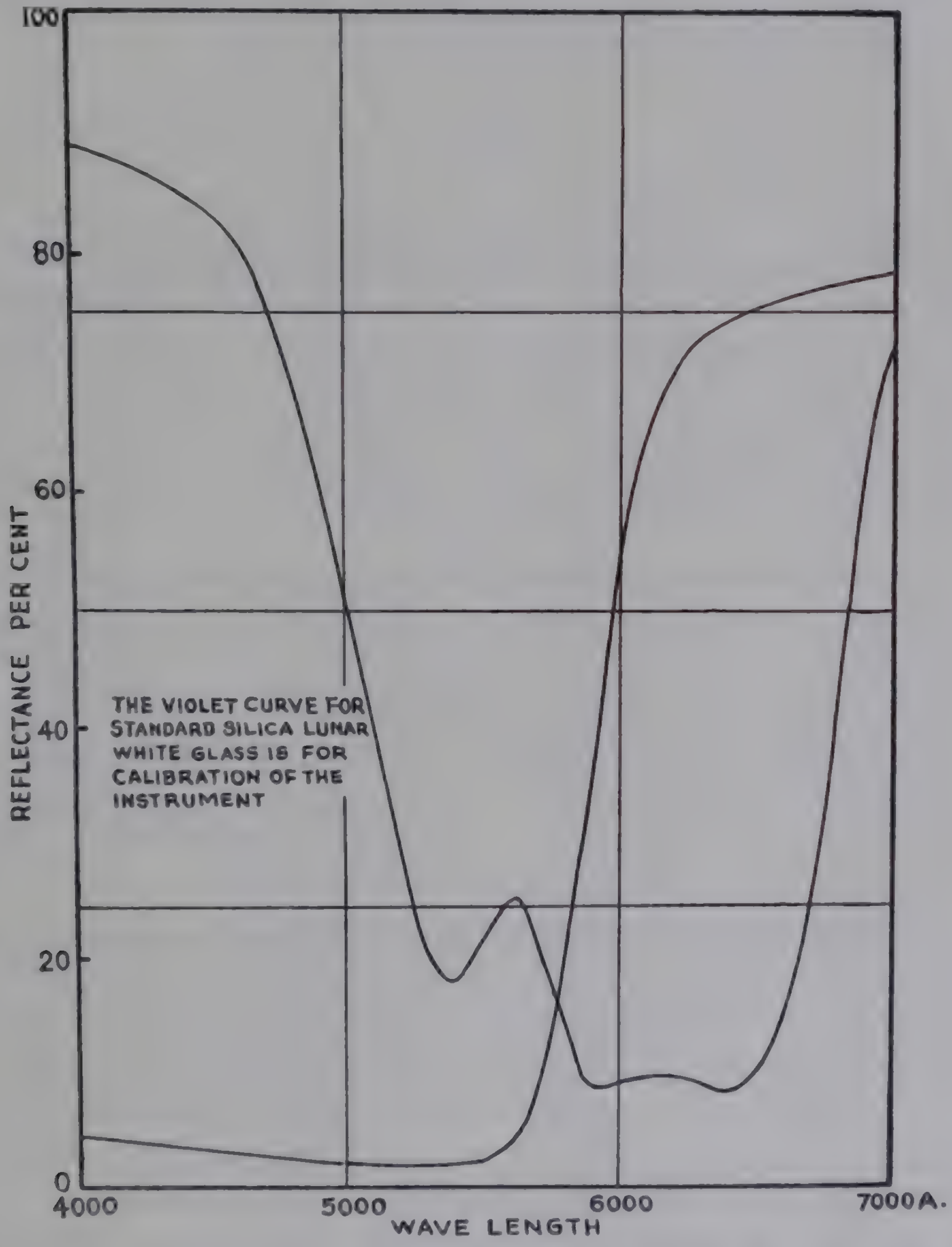

Fig. 2. Spectral reflection curve of a cotton fabric dyed red (Naphtol AS and Scarlet GG) (Wright).

Measurement of light absorption. The light absorption characteristics of a substance are measured by a spectrophotometer, which is a photometric arrangement attached to a spectrograph.[2] For a study of the color distribution attention is confined to observations over the visible spectrum. With such an instrument records are made of the intensity of the transmitted (or reflected) light in comparison with the intensity of the incident light at very short intervals of wave lengths. Spectrophotometric measurements can be made visually or photographically or photoelectrically. Automatic recording instruments using photoelectric devices are also available.

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[2] Brode, Chemical Spectroscopy, 2nd ed., Wiley, New York, 1943.

The relationship between the incident and the absorbed radiation at a given wave length is expressed by Lambert's law (i),

$$I = I_0 \, e^{-kd}; \quad \text{or} \quad E = \log \frac{I_0}{I} = 0.4343 \; kd \qquad \text{(i)}$$

where E is the "extinction" or "density," I_0 and I the intensity of the incident and the transmitted (or reflected) light respectively, k the absorption constant of the medium, and d its thickness in centimeters. For solutions in a solvent of negligible absorption the law (i) is modified by introduction of a factor for the concentration of the solute. The final expression (Lambert-Beer law) then reads in its conventional form (ii), in which ε, the molecular extinction coefficient, replaces the absorption

$$\log \; I_0/I = \varepsilon ct \qquad \text{(ii)}$$

constant k of (i), c is the concentration of the solute in moles per liter, and t is the thickness of the solution in centimeters. The ratio $\log \frac{I_0}{I}$ is the "optical density" of the medium or the solution, from which the transmission factor can be worked out. Thus a medium having optical density at a given wave length equal to 0, 1, or 2 has transmission factors 1, 0.1, or 0.01; or 100, 10, or 1% transmission respectively.

For transparent materials and more particularly for solutions the usual record is an absorption curve, where the molecular extinction coefficients ε, calculated from the Lambert-Beer law, are plotted against (1) the wave length λ; or (2) the wave number $\nu = 1/\lambda$ (number of waves in a centimeter); or (3) the frequency c/λ (c is the velocity of light, 3×10^{10} cm. per sec.). The fresnel F (vibrations per second $\times$ 10^{-12}) is used as the unit of frequency. Where the extinction coefficients cover a wide range (e.g., from 10 to 100,000), log values are conveniently plotted on the ordinate. The advantage of plotting wave lengths on the abscissa is that one can visualize exactly the location of the absorption band in the region under investigation. On the other hand wave number or radiation frequency units are advantageous, when definite quantitative regularity in the spacings, as in the fine structure of an absorption band or the relative shift of an absorption band, is to be noted in the investigation of molecular structure. Table II shows the wave numbers and frequencies for several wave lengths of light in the visible, near, and middle ultraviolet regions of the spectrum.

TABLE II

WAVE LENGTHS, WAVE NUMBERS, AND FREQUENCIES

Wave length A.	*Wave number* cm.$^{-1}$	*Frequency* *Fresnels*
8000	12500	373
7000	14286	429
6000	16666	500
5000	20000	600
4000	25000	750
3000	33333	1000
2000	50000	1500

The light absorption curve of a colored substance in the visible range of the spectrum, when converted into the corresponding reflection (or transmission) curve, gives the precise proportions in which various components make up the total color. Such a curve specifies the color of a substance in a unique manner.

For the surface color of opaque objects spectrophotometric observations are usually recorded as a curve of which the ordinate indicates either the optical density or the reflection factor and the abscissa the wave lengths of the incident light. In the Hardy Recording Spectrophotometer, made by the General Electric Co., white light is split as usual into its components by means of a prism, but by an automatic device successive wave lengths of light fall on the pattern, and the reflected light is measured photoelectrically and continuously recorded on a rotating drum. Figure 3 gives the spectral reflectance curves obtained on the Hardy instrument of two green fabrics matched in daylight. Each curve defines the color of the pattern uniquely, and Fig. 3 illustrates the fact that a pattern which may appear to be a match as observed visually in daylight will give a different curve if the shade has been produced by a different dye or mixture of dyes. Under different lighting conditions a pattern with a single peak in the reflectance curve usually appears the same color, whereas a color change is observed in a pattern with two distinct peaks.

Other methods of color specification employing types of instruments which are different from the spectrophotometer and simple to handle are discussed later. Apart from their utility in color specification, light absorption measurements in the visible range when combined with those in the infrared and in the ultraviolet regions provide fundamental data on the molecular structure.[3]

Changes in absorption spectra produced by constitutional changes in a molecule may involve a shift in the frequency or a change in the intensity of absorption or both. These effects are usually defined by certain terms.

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[3] See Chapter VIII.

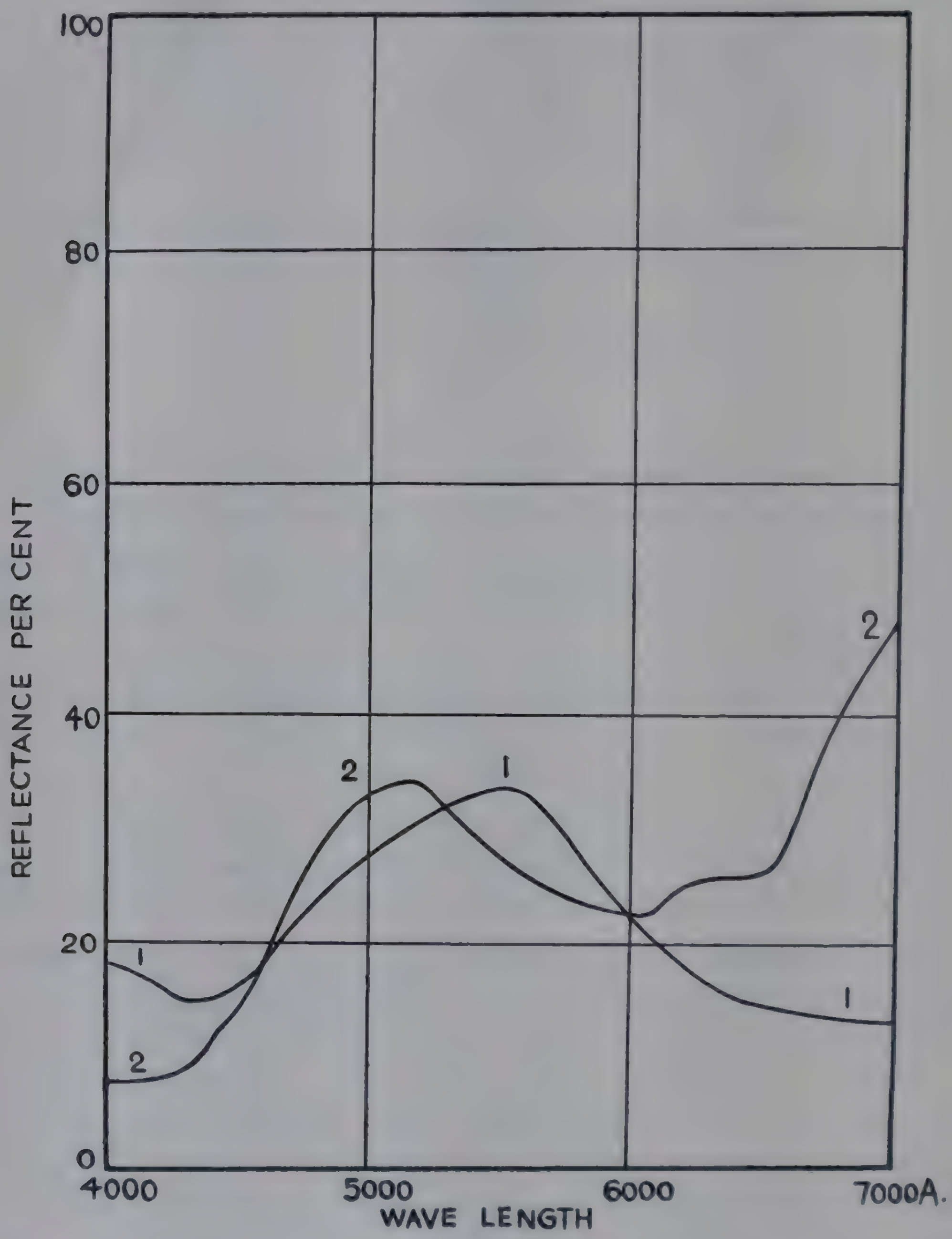

Fig. 3. Spectral reflection curves of two green fabrics dyed with (1) Naphthol Green B 1.74%; (2) a mixture of Acid Violet 4BC 0.076%, Xylene Fast Yellow 2GP 0.74%, Disulphine Blue VS 0.56%, and Xylene Fast Orange PO 0.02% (Wright).

A *bathochromic* effect is a shift of the absorption band towards lower frequencies, corresponding therefore to a deepening of the color from yellow, through red and blue, to green. The opposite effect, representing a lightening of color or a shift of the absorption frequency towards higher frequencies, is described as *hypsochromic*. A *hyperchromic* effect is an increase in the intensity of absorption, i.e., in the extinction coefficient of an absorption band; and the opposite effect is *hypochromic*.

The human eye and color vision. The eye brings the light and color of the world into human experience. Apart from the retina, the eye is of simple construction and consists of the cornea, the iris, and the lens. Refraction of light by the cornea and the lens focuses the image of the object viewed on the retina, while the iris regulates the quantity of light admitted for distinct perception, its function being very much the same as that of the iris diaphragm of a camera. The lens has the power of accommodation, and by the reflex action of alteration in its curvature it brings the objects beyond 24 cm. automatically into focus. It is corrected for spherical aberration, but not for chromatic aberration. On account of the latter defect a greater muscular effort is necessary to focus a red object on the retina than a blue. A sense of shorter distance is associated with muscular effort, and an optical illusion is created when a red and a blue object similar in size and placed at the same distance are viewed together. The red object appears to be smaller because it is imagined to be further away.

Rods and cones. The retina, which lines the inner periphery of the eye socket, is made up of several layers of cells covered with optic fibers, all of which lead through a central optic nerve to the brain. Important elements which endow the eye with the faculty of vision are present in the last layer of the retina and are known as the rod and cone elements because of the shape of the posterior parts of the characteristic cells distributed in the ultimate retinal layer. They secrete colored fluids, and from the retinal rods a rose-colored substance, visual purple or rhodopsin, has been isolated; it is a conjugated protein in which the prosthetic group is a vitamin A derivative, and it fades to a pale yellow in the light with conversion into vitamin A aldehyde.[4] The color returns in the dark, but there is a certain minimum period before it does so to the full extent, the time lag being necessary for the eye to see objects in the dark or become "dark-adapted." "Dark adaptation," the lack of which represents night blindness, is related to the continuous supply of vitamin A in the form of visual purple to the retina of the eye. A low vitamin A level diminishes the dark adaptation of the eye, which can therefore be utilized for diagnosis of vitamin A deficiency.

The light transmission characteristics of the rod and the cone elements are different. Although both have a maximum symmetrical transmission of about a wave length of light, this maximum lies at $\lambda 5{,}100$A. in the blue-green region for the rods and at $\lambda 5{,}550$A. in the green for the cones (Fig. 4). The response curves so obtained are known as the scotopic and the photopic curves of vision. In ordinary daylight and up to a general illumination corresponding to 0.1 candle per sq. ft. photopic vision prevails, whereas considerably below this range at 0.0001 candle per sq. ft. scotopic vision is operative. In subdued light, therefore, the rod elements are more active, the sense of color is lost, and colored objects assume a grey appearance.

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[4] Wald, *J. Gen. Physiol.* **21**, 810 (1938); Morton, *Nature* **153**, 69 (1944).

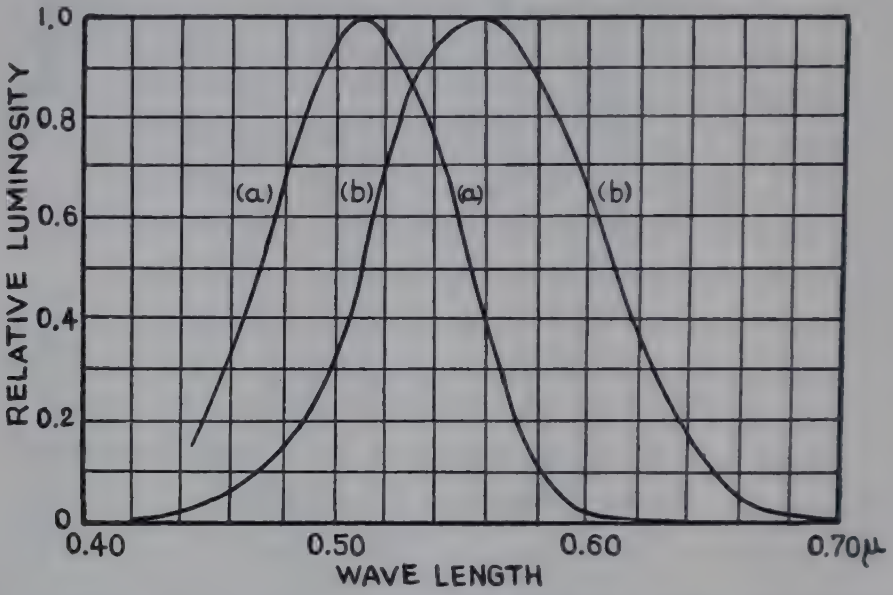

Fig. 4. The equal-energy luminosity curve (*a*) for rod vision, as measured at low intensities in the extrafoveal area of the retina; (*b*) for cone vision, as measured at high intensities at the fovea (Wright).

However brightly colored objects may be during the daytime, they appear grey by weak illumination as at twilight. Distinct perception of color therefore requires lighting which has as its lower limit a value of about 10^{-1} candle per sq. ft., when the photopic or color vision starts functioning through the cone elements. All the colors to which the eye responds are thus

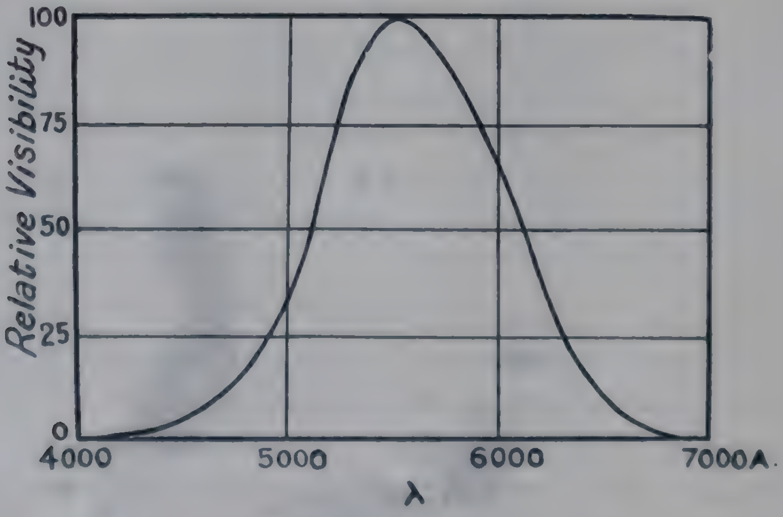

Fig. 5. Visibility factor (Murray and Spencer).

brought into human experience only by the presence of the cones in the retina. The normal response curve of the eye in daylight (visibility factor) for the individual wave lengths in the visible spectrum is almost identical with the photopic curve of the cones (Fig. 5). Change to scotopic vision with greater sensitivity in the blue-green (the Purkinje effect) takes place below the threshold illumination of about 10^{-4} candle per sq. ft.

Trichromatic theory of color vision. Any color except white can be reproduced by a suitable mixture of two or three primary colors (red, yellow, and blue), with use in some cases of a negative quantity of one primary color. Mixtures of the first two give various tints of orange; the second and the third produce all types of greens; the first and the third give purples. Mixtures of all three in suitable proportions give different shades of grey, the darkest of which is black. These effects accord with the subtractive law of color mixture, whereby a color sensation is produced as a result of absorption or subtraction of certain colors in the spectrum and selective reflection or transmission of others, as discussed earlier. On the other hand, when colored beams of light are mixed and scattered by a nonselective material, such as a magnesium oxide block or a white fabric, the color sensations produced follow the additive law of color mixtures. The three primaries for additive mixture are red, green, and blue, and they must be so chosen that each covers approximately a third of the visible spectrum. A mixture of red and green in the additive system produces a yellow sensation, and a mixture of all three primaries in the right proportions produces the sensation of white. In the subtractive system each primary absorbs approximately a third and reflects or transmits two-thirds of the visible spectrum. Subtractive systems of color photography use magenta, yellow, and blue-green as the most suitable subtractive primaries. A mixture of magenta and blue-green, for instance, leads to blue in the subtractive system.

Since color vision is due to the cones it is assumed that three types of distinct mechanisms are connected with them, corresponding approximately to the red, green, and blue sensations.[5] It is not known whether there are three sets of such cones or whether each cone contains all the essential mechanisms for three individual responses. Possibly the cones hold colored secretions similar to the visual purple in the rods, but sensitive to radiations with maxima in the red, green, and blue regions only. The three mechanisms are independently stimulated by a color in proportion to the amount of the three fundamental components making up the total color. The three stimuli are again compounded in the brain with the result that the synthetic image of color made up from the three sensations appears to the eye in its natural color. The process is similar to color reproduction in printing. In its simplest form this consists in photographing the colored object separately with three color screens corresponding to the three primary colors and in printing the picture of the object successively with three blocks, with use of yellow, magenta, and blue-green transparent inks, so that the prints are superimposed. If the original colors of the object are distributed over the three primaries in the right proportions, a nearly faithful reproduction can be obtained.

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[5] The trichromatic theory of color vision is not universally accepted; cf. *Nature* **162**, 639 (1948); Stiles, *ibid.* **160**, 664 (1947).

Color blindness. Additional support for the trichromatic theory of color vision is obtained by the phenomenon of partial or total color blindness. Persons who have total color blindness see only various shades of grey where the normal eye sees the colors red, green, and blue. The blindness may be only for one of the three primary colors, and the person so affected is called a dichromat, since he sees only two colors. A monochromat sees only one color; persons with normal color vision are trichromats. Most color-blind persons are dichromats. Among the dichromats there are subdivisions, the red-blind (Protanopes), the green-blind (Deuteranopes), and the blue-blind (Tritanopes). Tritanopes are very rare. Figures available for European countries show that color blindness, which is usually a hereditary defect, occurs in 8% of men and 1.5% of women. The usual test for this malady is to find the ability of a person to make out certain figures in a mosaic pattern consisting of grey and colored spots of various sizes. Ishihara's charts for color-blindness tests, employed for naval recruitment, are of this type.

The trichromatic theory of color vision gives a simple explanation of color blindness. Failure of one or more of the three cone mechanisms, responding to red, green, and blue light stimuli, leads to a loss of the color sense corresponding to the defunct mechanism.

MEASUREMENT OF COLOR

We may now consider how the color of an object can be measured quantitatively and specified in unambiguous terms. Reference has already been made to the unique manner in which color specification can be made by means of the light absorption or reflection curve in the visible spectrum. This method has the advantage of being independent of the nature of the light source, for it specifies the amount of absorption at all wave lengths of visible radiation. In connection with practical problems of color, however, methods of color measurement are often employed, which are based on the trichromatic theory of color vision. If the primaries chosen are red, green, and blue, a color sensation can be specified as consisting of these three colors in a definite proportion. Combination in any other proportion would result in a sensation different in its color qualities.

Three wave lengths in the visible spectrum corresponding to the three primary standards are selected, and the coefficients for each of the two or three of these primaries which are necessary for obtaining color matches for the full range of colors in the spectrum are determined. A suitable instrument is the Wright trichromatic colorimeter. The results are plotted in the form of three coefficient curves (Fig. 6). It is observed that for certain colors, notably reds and greens, a definite proportion of the primaries has to be added to the spectral colors themselves before a match can be obtained. In parts of the red and green sensation curves, therefore, the coefficients have negative values, and to avoid this inconvenience the coordinates are changed so that the coefficients for the primaries take positive values. By this change of coordinates the primaries are also changed and do not then correspond to any known spectral colors, though the nature of the sensation remains the same. Corresponding to the red, green, and blue, the new primaries ("tristimulus values") are designated by the symbols, X, Y, and Z, respectively. The trichromatic unit equation is then put down as: $C = xX + yY + zZ$ where $x + y + z = 1$; and for the white: $0.333\ X + 0.333\ Y + 0.333\ Z = S_E$. Any color may thus be defined uniquely by its trichromatic coefficients, if its brightness is measured independently by reference to a standard white substance such as magnesium oxide. The method now adopted incorporates the brightness factor in the coefficient for the Y sensation, corresponding to the green, by making

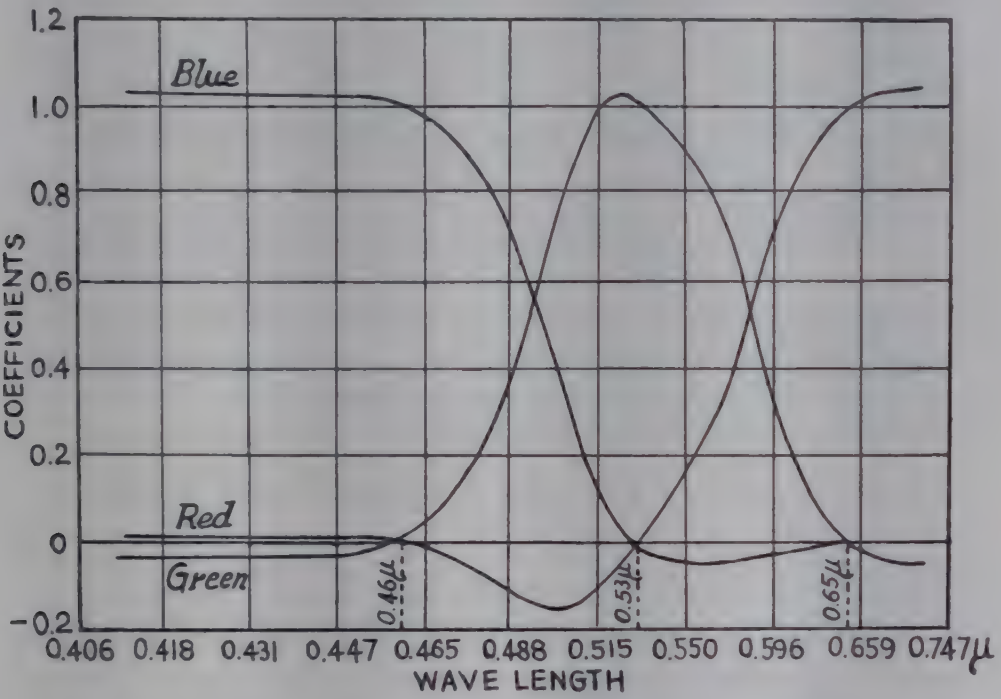

Fig. 6. Mean coefficient curves from results of ten observers (Wright).

the X and Z sensations devoid of any brightness, and these primaries are specified by the International Commission on Illumination as X, Y and Z.[6]

The chromaticity diagram. The color values can be shown on a diagram having the form of an equilateral triangle: the color triangle. The points at the three corners then correspond to the three primary sensations X, Y, and Z. The sides of the triangle represent various mixtures of the two components XY, YZ, XZ, whereas points within the triangle indicate various colors with definite values of x, y, and z. The white with equal values of the primaries is located at the center of the triangle. When spectral colors are plotted on this diagram a continuous curve, the spectrum locus, is obtained which closely follows part of the sides YZ and XY. The purple colors along the XZ side are missing in the locus since these are not present in the spectrum. In place of the color triangle it is more convenient to adopt the ordinary system of two coordinates representing x and y, since the third value z can always be obtained from the unit equation. The spectrum locus can then be plotted on this system as the chromaticity diagram, in which all the colors are located (Fig. 7).

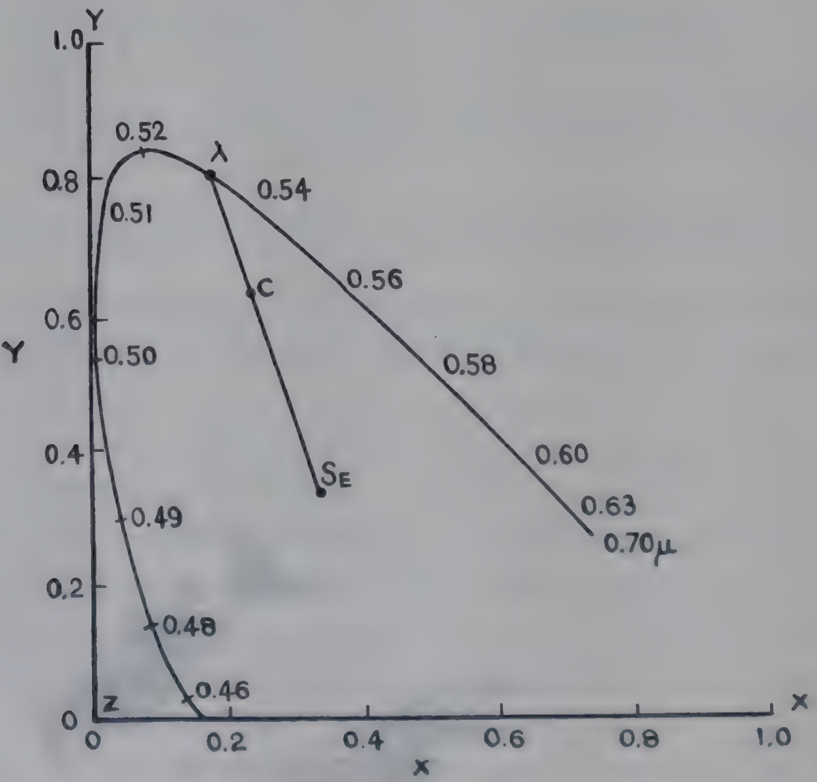

Fig. 7. The locus of the spectrum colors in the XYZ chromaticity diagram and the description of a color by reference to the locus and the white point *SE* (Wright).

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[6] From brightness data for many dyes of different hues, Vickerstaff concludes that those having only one absorption band edge in the visible spectrum are brighter than those with two; *Proc. Phys. Soc. London* **57**, 15 (1945).

An instrument employed for direct determination of the trichromatic coefficients is a trichromatic colorimeter; the color of the sample is matched visually or by a photocell against a mixed beam of colored lights. The light source is a tungsten filament lamp, on which the voltage is kept constant so that its intensity does not vary during the measurements. Three separate beams of red, green, and blue color are obtained by means of suitable filters. The intensity of each beam is controlled by adjustable apertures. The instrument readings obtained with each of the three primaries employed, when the pattern (illuminated by one of the standard light sources A, B, or C) is matched, are converted into trichromatic coefficients from the calibration factors of the instrument, which take into consideration the energy distribution values of the standard light source as well as the transmission qualities of each of the filters.

The trichromatic coefficients of a colored sample, although they give a unique specification of its color, do not afford the detailed information available from the spectrophotometric absorption curve. On the other hand these coefficients can be evaluated from the absorption curve when the reflection (or transmission) factors of the test sample at short intervals in the spectrum are employed to calculate the energy values of each of the three primary stimuli for the illuminant used. The spectrophotometric method is therefore preferable for the measurement of color wherever possible, and the results are expressed in both forms. The chromaticity diagram can next be used for location of the point corresponding to the color measured (point C, Fig. 7). If the " white " point S_E corresponding to the illuminant employed for the measurement is also marked on the diagram, the line joining the two points will cut the spectrum locus at a point representing a definite wave length of light and corresponding to the dominant hue of the material under test. Further, the purity of this color, which is the amount of its admixture with white, will be given by the ratio of the distance between the white point and the sample point to the distance between the sample point and the point of the dominant wave length. Thus a color can also be specified in terms of the dominant wave length (or hue) and of its purity (Fig. 7).

The Munsell and the Lovibond systems. Color specifications based on an arbitrary system of color measurement are often employed in trade. One is the Munsell system which is represented on a three-dimensional figure, the Munsell Tree.[7] The vertical " stem " of this tree is conveniently divided into ten equal parts, the lowest being black and the highest white. Intermediate parts from the top to the bottom are shades

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[7] Munsell Book of Color, Standard Ed., Munsell Color Co. Inc., Baltimore, Md., 1929.

of grey which progressively become darker. Each of the "branches" perpendicular to the stem represents a color or hue, whereas the distance from the stem along each branch indicates the purity or "chroma" of color characteristic of the branch. The greater the distance from the stem, the greater is the purity of the color. Although an infinite number of colors from red to purple on any horizontal circular section of the tree is possible, in practice only ten main segments of the circle are provided (R, YR, Y, GY, G, BG, B, PB, P, and RP, the symbols having obvious meanings). Each of these ten segments is again divided into ten parts, so that in all there is a provision for 100 colors from red to purple. These when combined with ten grey "values" on the stem and twelve chromas on each branch can be calculated as $100 \times 0 \times 12 = 12{,}000$ colored patterns; but since many spectral colors are unsaturated, their chroma figures are low, and the actual number of Munsell patterns which can be realized in practice is at the most half the calculated number. These are sufficient for ordinary requirements. Thus a blue-green sample matching with a Munsell pattern located in the fifth section of the stem along the middle of the branch BG is specified as BG 5/6, i.e., a blue-green color with value 5 and chroma 6. Figures 8 and 9 show the vertical and horizontal sections of the Munsell Tree.

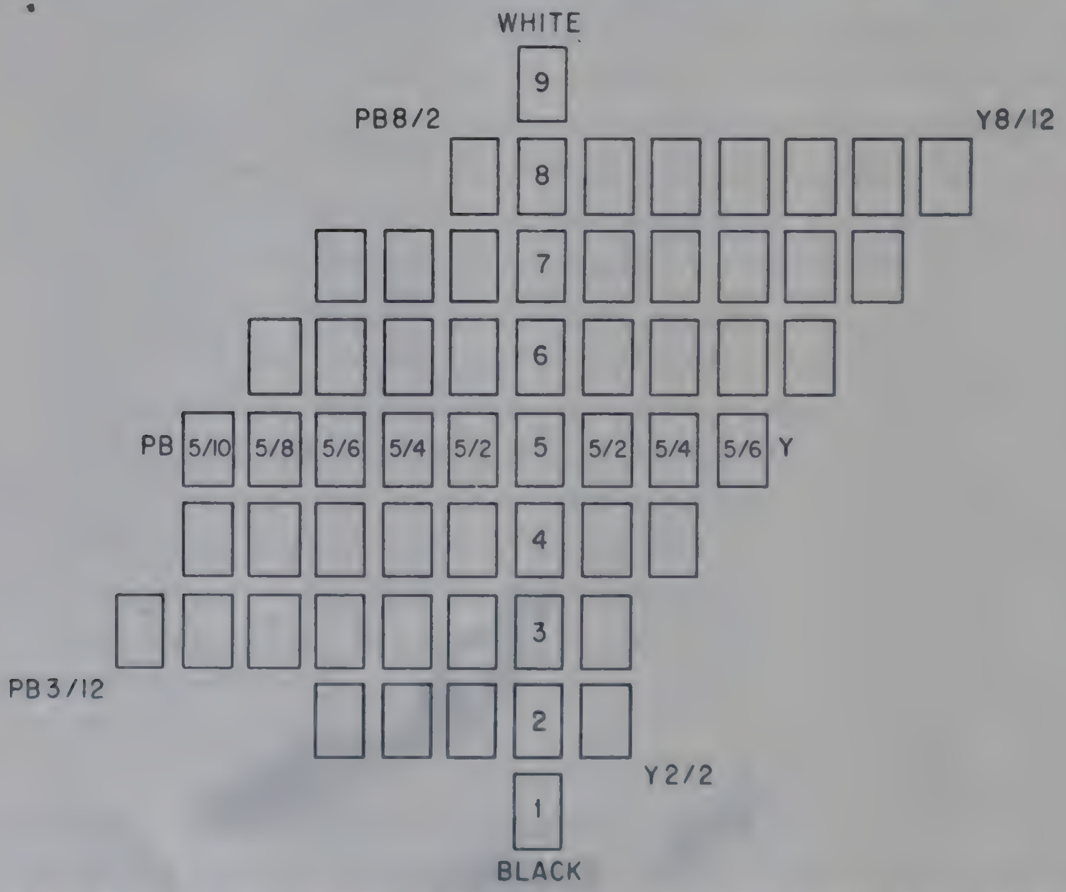

Fig. 8. A vertical section through the Y-PB plane of the Munsell Tree (Wright).

Another arbitrary system of color nomenclature is the Lovibond system. Color measurements on this system are carried out in a simple instrument, the Lovibond Tintometer, which employs the subtractive method of color matching. The color of the test piece is matched with a beam of "daylight" reflected by a standard white surface and passing through a series of red, yellow, and blue glasses as necessary. The colored Lovibond glasses for each of the three colors are numbered from 0.1 to 18 units, the amount of tint in a series being proportional to the number of units. The result is expressed in the total number of units of one or more colors required for the match. A recent modification of this tintometer makes it possible to convert the Lovibond units into the trichromatic coefficients by conversion factors and charts.

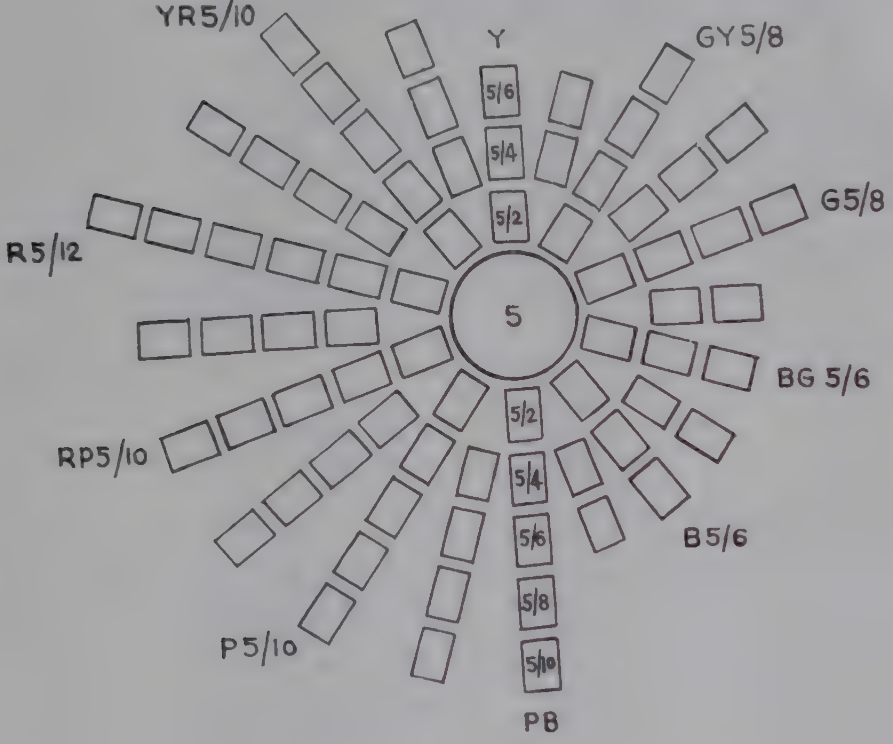

Fig. 9. A horizontal section through the value 5 plane of the Munsell Tree (Wright).

A few color specifications based on various systems of color measurement are given in Table III for nine common colors. The specifications are drawn from recent literature on color.[8]

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[8] British Color Council's Dictionary of Colors, London, 1934; Textile Color Card Association Standards, Reimann, Judd and Keegan, *J. Optical Soc. Am.* **36** 128 (1946).

TABLE III

SPECIFICATIONS OF SOME COLORS ACCORDING TO VARIOUS SYSTEMS OF COLOR MEASUREMENT

Color (Common name)	*Description*	*B.C.C. No.*	*T.C.C.A. No.*	*I.C.I. Specification*			*Munsell Notation*		*Lovibond units*		
				x	y	Y	*Hue*	*Value chroma*	R	Y	B
Coral	Vivid pink	182	70206	0.426	0.314	0.450	2.5 R	7.1/10.6	4.5	1.8	0
Marigold	Strong reddish orange	56	70071	0.555	0.386	0.264	1.6 YR	5.7/13.8	8.5	17.0	0
Lemon	Moderate yellow	52	70205	0.424	0.443	0.603	4.7 Y	8.1/8.7	1.9	13.0	0
Nile	Pale yellow-green	21	70031	0.339	0.378	0.508	4.9 GY	7.5/3.3	0	1.7	1.0
Pistachio	Weak yellowish green	9	70032	0.311	0.371	0.370	0.4 G	6.6/3.6	0	3.0	3.0
Jungle green	Very dark green	27	70132	0.267	0.337	0.042	1.1 BG	2.4/2.7	3.2	7.9	8.9
Blue turquoise	Light greenish blue	118	70021	0.239	0.293	0.340	2.7 B	6.3/5.6	0	2.2	4.7
Royal blue	Dark purplish blue	197	70087	0.195	0.153	0.041	6.9 PB	2.3/8.4	1.1	0.8	11.0
Lavender	Pale purple	176	70055	0.300	0.271	0.300	5.5 P	6.0/4.8	1.5	0	0.9

CHAPTER VIII

COLOR AND CHEMICAL CONSTITUTION

Inorganic compounds which exhibit deep color are ionic and complex compounds of the transition metals, substances containing an element in two different oxidation states, and nonionic molecules in which there is a direct linkage between heavy atoms. Among organic compounds, aliphatic compounds are in the main colorless, and deep color is encountered only in the derivatives of benzene, naphthalene, anthracene and other aromatic ring systems.

EARLY THEORIES[1, 2]

Graebe and Liebermann noticed (1868) that all the colored organic compounds which were then known were decolorized by the addition of hydrogen, and they concluded that color was due to *unsaturation* or "a closed internal linkage," particularly connected with oxygen or nitrogen atoms.

Chromophores and **auxochromes.** Witt put forward (1876) the theory of *chromophores* and *auxochromes*, which stated that all colored organic compounds contain chromophoric groups which are responsible for the color; auxochromic groups intensify the action of the chromophores and give the colored compounds dyeing properties. As examples of chromophores he mentioned the NO_2, NO, N=N, and CO groups. He regarded auxochromes as weakly salt-forming groups, e.g., NH_2, NHR, NR_2, and OH; and strongly salt-forming groups, whether they are acidic or basic (e.g., SO_3H, COOH, NR_3), were considered to have no auxochromic properties, and in fact to diminish the color. A compound containing a chromophore may be colored, but unless an auxochrome is also present, it will not function as a dye for a textile fiber (cf. benzene, trinitrobenzene, phenol, and picric acid). Witt called a chromophore-containing compound a *chromogen*. The color of a chromogen, as elaborated by later users of Witt's theory, depends on the nature, number, and position of the auxo-

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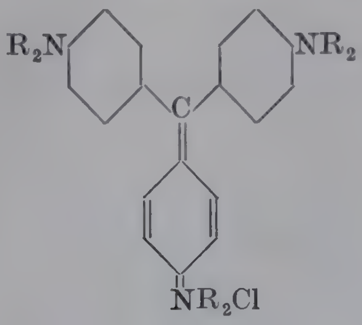
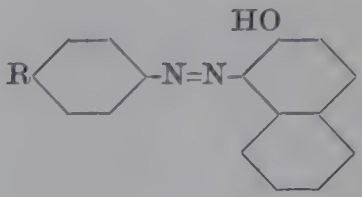
[1] Watson, Color in Relation to Chemical Constitution, Longmans, London, 1918.

[2] Henrich, Theories of Organic Chemistry, Wiley, New York, 1922: Martinet, "Couleur et Constitution chimique," Traité de chimie Organique; sous la direction V. Grignard; Secretaire General, Paul Band, Tome II, Fascicule II, 653 (1936); Ramart-Lucas, "Structure des molecules et spectres d' absorption," *ibid.* Tome II, Fascicule I, 59 (1936).

chromes. The influence of the first factor is shown by the colors of Pararosaniline (red), Crystal Violet, and Aniline Blue (I; $NR_2 = NH_2$, NMe_2, and NHPh). Watson[1] has tabulated the colors of the hydroxyanthraquinones and their salts in illustration of both the second and third factors. Further, the dyeing properties of a chromogen containing an auxochrome may be completely altered by introduction of other groups; thus the benzeneazo-β-naphthol derivative (II) is an insoluble azo color produced on the fiber, or an acid color, or a basic color according as R is H, SO_3Na or NMe_2. Liebermann and Kostanecki (1885) also distinguished between color and dyeing properties when they stated their " rule " that at least one hydroxyl *ortho* to a chromophoric group is necessary for giving a substance mordant-dyeing properties.

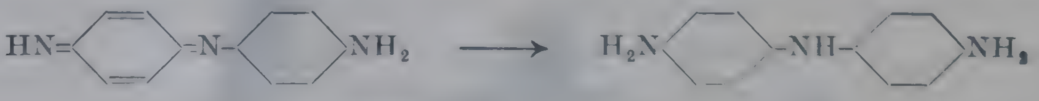


(I)



(II)

The quinonoid theory. In 1888 Armstrong postulated that dyes are derivatives of quinones in which one or both the oxygen atoms may be replaced by other atoms or groups, and the color of dyes is due to the quinonoid structure. Although the quinonoid theory consisted essentially in a new and closer definition of Witt's chromophore, it serves to explain in a simple and rational manner some of the important empirical facts of dyestuff chemistry. The majority of colored organic compounds and dyes in particular can be represented in quinonoid forms. Many dyes are sensitive to reduction, the reaction being similar to the conversion of yellow *p*-benzoquinone to colorless hydroquinone; such dyes undergo reduction to their leuco compounds, e.g., the blue indamine (III) to the colorless diaminodiphenylamine (IV). The quinonoid hypothesis leads to a distinction to be anticipated between *o*- and *p*-quinonoid dyes. The leuco compounds of some groups of dyes (e.g., azines, acridines) are readily reoxidized, even by atmospheric oxygen. The leuco compounds of certain



(III) (IV)

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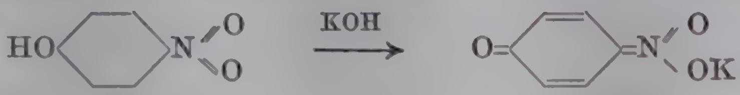
[1] See p. 323.

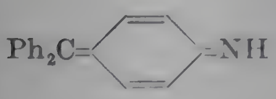
other dyes (e.g., triphenylmethane derivatives, indamines, indophenols) require more powerful oxidizing agents (dichromate, persulfate, etc.) for regeneration of the original quinonoid dye, thus simulating the behavior of hydroquinone. Such behavior on reduction and reoxidation is indeed one of the fundamental reactions on which schemes for the identification of dyes are based.

Apart from its obvious limitation that it makes no attempt to explain why a quinone should be colored, the quinonoid theory has well-known exceptions and difficulties, such as the color of azobenzene and the behavior of anthraquinone derivatives on reduction and reoxidation.

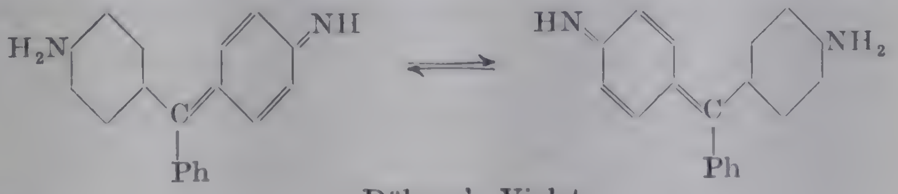
Hantzsch (1907) explained the deepening of color when *o*- or *p*-nitrophenol is converted into an alkali salt as being connected with the structural change of the phenol (V) to the quinonoid aci-form (VI). In confirmation of his view regarding the tautomerization of the nitrophenols, Hantzsch was able to isolate colored (red) alkyl ethers corresponding to the aci-form in addition to the colorless ethers, the former being unstable and readily isomerizing to the colorless form. Hantzsch took the view that color is an additive property, and that since the simultaneous presence of the NO_2 and ONa groups produces visible color, which neither produces separately, there must be an interaction between the two groups, resulting in a new structure for the molecule. He therefore regarded change of color as evidence of change of structure, and he termed the phenomenon "chromoisomerism." For instance, he assigned specific bands in the absorption spectra of the diphenylviolurates to the nitroso and isonitroso forms.[3] Baeyer[4] explained the conversion of the colorless fuchsonimine to the deeply colored Döbner's Violet by the introduction of an amino group as a result of oscillation of the quinonoid condition between the two benzene rings.



(V) (VI)



Colorless fuchsonimine



Döbner's Violet

Soon after Witt's theory, Nietzki (1879) postulated that the color of a dye could be deepened (from yellow through red to green) by adding groups to increase the molecular weight. While "Nietzki's rule" is often valid, it is the nature and not merely the weight of an added group on which the deepening of color depends. In the homologous series $CH_3(CH_2)_a$–X–$(CH_2)_bCH_3$, in which X is a chromophoric or absorbing group, the depth of the color is independent of the numbers *a* and *b*.

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[3] Hantzsch, *Ber.* **43,** 666 (1910).

[4] *Ann.* **354,** 152 (1907).

Hewitt and Mitchell[5] made the important observation, on the basis of their work on the absorption spectra of azo dyes, that the " chief oscillation frequency is less, and consequently the color is deeper, the longer the conjugate chain." After submitting " Hewitt's rule " to extensive experimental tests, Sircar concluded that the depth of color is proportional to the length of the conjugate chain in the part of the molecule containing the auxochrome.[6] According to Watson and Meek[7] " dyes which are quinonoid in all possible tautomeric forms have a deep color, no matter how simple their structure or how small their molecular weight "; and the color is deeper the longer the conjugate chain reversed in the tautomeric change. " A pulse passes in one direction along the conjugate chain . . . and back again; . . . this pulse is the vibration which causes the color of dyes." In ionized dyes, " there is no vibration of the atoms of the molecule, but only rhythmic arrangement of the strains in the molecule. Even when the substance is not ionized, the only atom that must necessarily move is the hydrogen atom concerned in the tautomerism."

Dilthey and Wizinger's theories. Dilthey and Wizinger[8] define chromophores as coordinatively unsaturated atoms, as distinct from Witt's unsaturated groups; the latter owe their chromophoric properties to the coordinatively unsaturated atoms which they contain. There is a marked increase in light absorption when there is a transition from a coordinatively unsaturated atom to the ionic state, and the most powerful absorbers of light are " ionoid " in character. The hypothesis that a strongly colored substance must be an ion or an inner salt is contrary to many facts. Neutral substances such as *p*-nitroaniline and 4-nitro-4′-aminostilbene, which are yellow to orange-red, lose their color or become pale yellow upon the addition of hydrogen ion. In the phenomenon of halochromism, the neutral organic compounds, which become brilliantly colored on the addition of hydrogen ion, are colored to about the same depth and intensity by the addition of neutral substances such as boron trichloride or stannic chloride instead of hydrogen ion.[9]

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[5] *JCS* **91,** 1251 (1907).

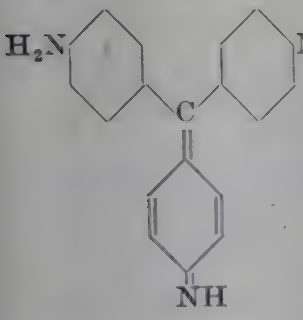
[6] *Ibid.* **109,** 757 (1916).

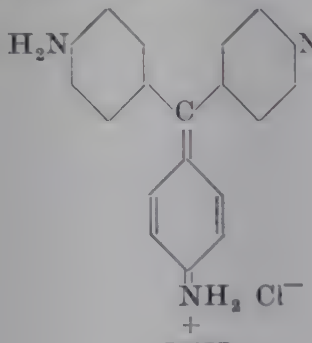
[7] Watson, *ibid.* **105,** 759 (1914); Watson and Meek, *ibid.* **107,** 1567 (1915).

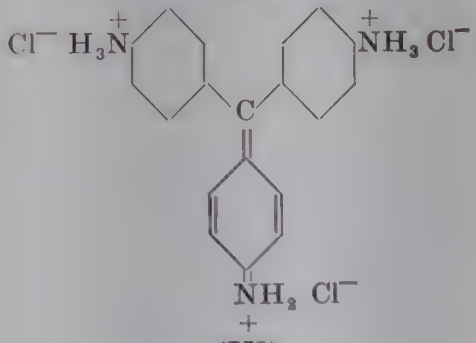
[8] Dilthey, *Ber.* **53,** 261 (1920); Wizinger, Organische Farbstoffe, Ferd. Dümmlers Verlag, Berlin u. Bonn, 1933; *J. prakt. Chem.* **157,** 1940 (1941).

[9] Lewis and Calvin, *Chem. Revs.* **25,** 273 (1939).

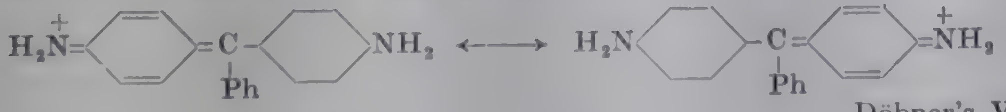
The Stieglitz theory. The contribution of Stieglitz[10] to color theory is a bridge between the older theories and the resonance concept of color. Since many dyes lose their color both by reduction and by oxidation, he considered them as being in an intermediate state of oxidation. They contained both oxidizing and reducing groups, identified respectively with chromophores and auxochromes. The result of the presence of the two in the molecule was intramolecular electron transfer. Valence electrons were therefore freed from the ordinary atomic restraints, and the absorption bands were shifted from the ultraviolet to lower frequencies, producing visible color. Color changes occurring on the addition of acid or alkali, as in the triphenylmethane dyes, were explained by Stieglitz as dependent on the salt formation increasing or decreasing the chromophoric or auxochromic character of the groups concerned. In the basic dyes such as those of the rosaniline series, when salt formation occurs by the addition of acid to (VII) in the oxidizing (quinonoid) component of the dye molecule, the color deepens (VIII); but when salt formation occurs with an auxochromic amino group and destroys its reducing power, the depth of the color is diminished (cf. IX).

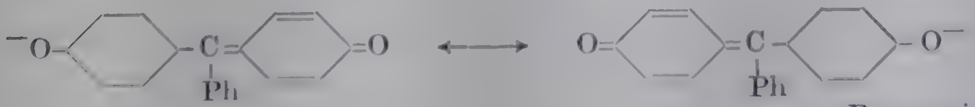

(VII)
Yellow


(VIII)
Red


(IX)
Yellow

Auxochromes and resonance. As early as 1914, Adams and Rosenstein[11] suggested that the color of Crystal Violet is due to the oscillation of an electron. Bury (1935) applied this idea to a series of dyes, which he represented by extreme resonance structures.[12] In the basic dyes the resonance is associated with the cation, and among the examples quoted by


Döbner's Violet


Benzaurin

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[10] *Proc. Natl. Acad. Sci. U.S.* **9**, 303 (1923); *J. Franklin Inst.* **200**, 35 (1925).

[11] *JACS* **36**, 1472 (1914); see also ref. 4.

[12] *JACS* **57**, 2115 (1935).

Bury, two are the ions of Döbner's Violet and Acridine Orange. In acid dyes such as benzaurin the resonance is associated with the anion. Bury explained that the function of an auxochrome is to introduce the possibility of resonance.

The problem of the color of dyes is of the utmost complexity, for a truly comprehensive theory of color should account for both the qualitative and quantitative aspects of the color of all the known types of colored organic compounds. Acid and basic colors represent two somewhat special types, and even from the purely qualitative aspect, they are liable to lead to an oversimplified and erroneous interpretation of the general relation between color and structure. Bury, for instance, has referred to gallacetophenone as a vat dye, and has attempted to ascribe similar structures to this substance and to the anthraquinonoid vat dye, indanthrone. In recent approaches to a theory of color, progressive variations of structure and color are being carefully studied, and attempts are being made to correlate quantum-mechanical calculations of the absorption of light of simple molecules and of conjugated systems with the observed spectra.

INTERPRETATION OF ABSORPTION SPECTRA

Attempts to correlate the absorption spectrum of an organic compound, especially a complex dye molecule, with its chemical constitution and its resonance states must be made with caution in view of a variety of complicating factors. The purity of the compounds has to be ensured, by no means always an easy matter in dealing with a dye; for instance, it is a long and laborious process to obtain a water-soluble azo dye chemically pure. Even an analytically pure dye may still consist of a mixture of molecular species: *cis-trans* isomers (e.g., in the case of azo compounds and stilbenes); azophenol-quinonehydrazone tautomers in the case of *o*- and *p*-hydroxyazo compounds; keto-enol, amide-iminoalcohol, and lactam-lactim tautomers; monomers and polymers. The absorption spectra of many dyes are affected by acid, basic, and amphoteric addition.

Absorption spectra having usually to be observed in solution, further complications arise. Carefully purified solvents have to be used, and a solvent that has uniform transmission throughout the region under examination and does not interact in any way with the solute is desirable. The influence of solvents on the absorption bands of a simple substance is illustrated in Fig. 1 (after Klingstedt).[13] Solvates are eliminated by the use of a saturated hydrocarbon solvent, e.g., *n*-hexane, but more often than not, dyes are insoluble in paraffin solvents. The two-electron covalent bond does not absorb light of wave length between 2,000–10,000A., and solvents consisting of saturated molecules such as water, ethanol, cellosolve, and dioxane can usually be employed. When chlorinated aromatic hydrocarbons, nitrobenzene, concentrated sulfuric acid, etc., are used as solvents, the complications due to the spectral characteristics of the solvents themselves, hydrogen bonding between solute and solvent, oxonium salt formation, and other kinds of interaction leading to new molecular species with absorption spectra different from those of the molecule under investigation have to be carefully borne in mind. In special cases, such as the triphenylmethane dye (X) in which the charge on the ion is distributed more on one end of the molecule than the other, the dielectric properties of the solvents can have a profound influence on the spectra (cf. Fig. 2).[14] The absorption of a nonionized dye is strongly affected by the solvent if a polar structure, with which the color is associated as explained later, is stabilized by the solvent. Thus Phenol Blue gives solutions which vary in color from reddish

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[13] *Compt. rend.* **176,** 1550 (1923).

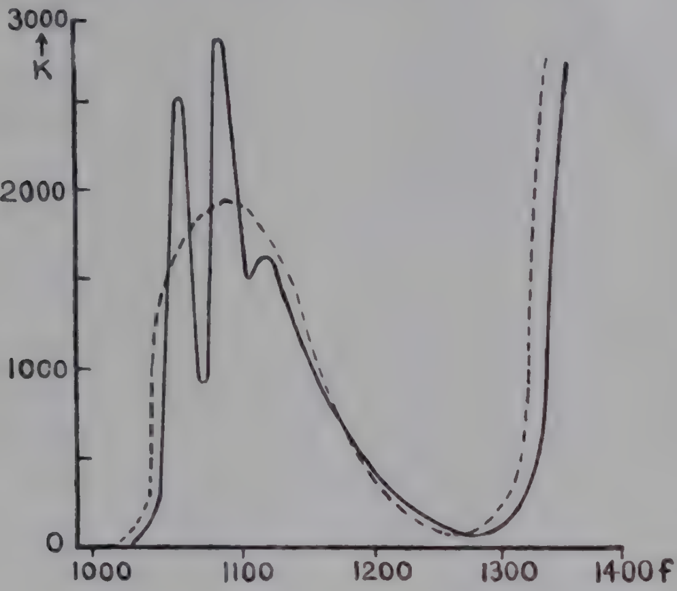
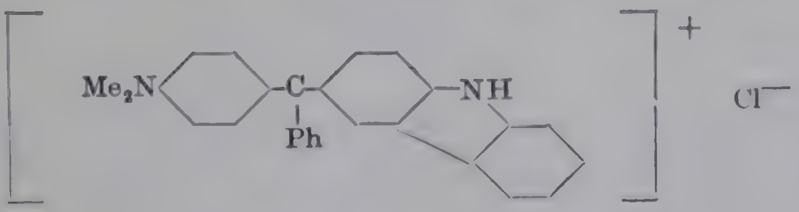


Fig. 1. Influence of solvents on absorption bands. Absorption of phenol in alcohol (————) and in hexane (————) (Klingstedt).



(X)

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[14] Branch, Tolbert, and Lowe, *JACS* **67,** 1693 (1945); see also Katzenellenbogen and **Branch,** *ibid.* **69,** 1978 (1947).

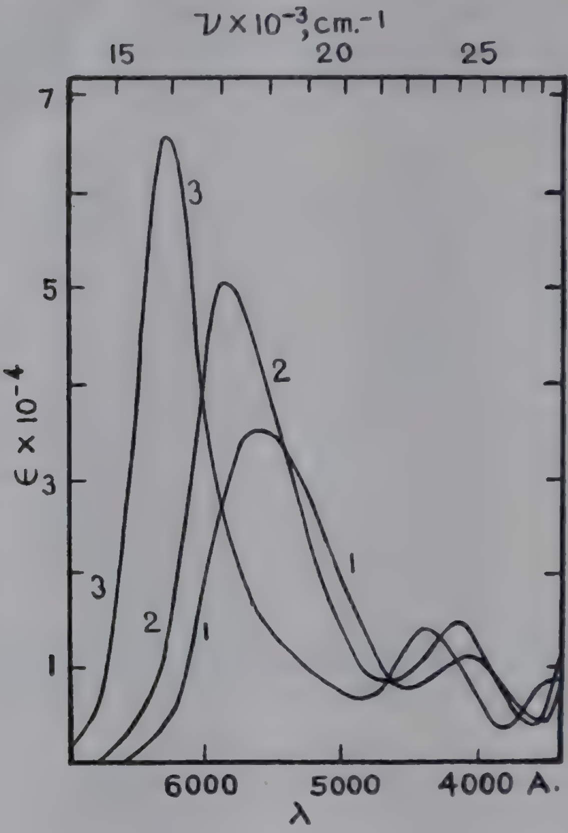
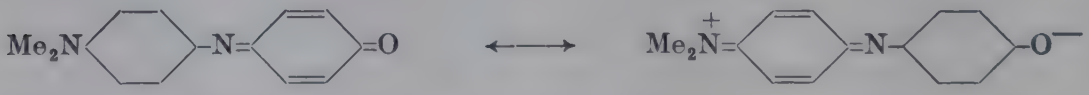


Fig. 2. Absorption curves for the dye (X) in (1) water, (2) methanol, and (3) chloroform.[14]

violet in cyclohexane to deep blue in water. The values of λmax vary from 5,520A. in cyclohexane to 5,820A. in acetone, 6,120A. in methanol,



(A) Phenol Blue (B)

and 6,680A. in water. The bathochromic shift corresponds with increasing dielectric constants of the solvents (2, 21, 31 and 80 approximately). Brooker and Sprague[15] have suggested that the resonance structure (B), associated with the deep color of Phenol Blue, is relatively unstable, but that it is increasingly stabilized by the dipole orientation of the surrounding solvent molecules as the polarity of the solvent is increased. The absorption bands of anthracene and phenanthrene undergo characteristic changes in wave length and intensity when different solvents are used, but the solvent effect does not appear to be connected with the dipole moment, refractive index, or density of the solvent.[16]

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[15] *JACS* **63,** 3214 (1941).

[16] Maddamo and Schnurmann, *J. Chem. Phys.* **17,** 108 (1949).

A substance obeys Beer's law if the curve obtained by plotting the molar extinction coefficients against wave lengths is independent of the concentration of the solution;[17] but many dyes do not obey Beer's law and the deviations vary with different types of dyes. The reversible polymerization of dye molecules is one reason for such deviations. Methylene Blue exists in considerable amount as the dimeric ion in a solvent of high dielectric constant such as water; in alcohol the dimeric band of Methylene Blue becomes pronounced at low temperatures; and in solvents of low dielectric constant molecular dimers and polymers are formed, the blue color changing to pink.[18, 19]

Using a substance in a single molar form and noninteracting nonabsorbing solvent, or taking into account the existence of more than one molecular species, separate electronic bands can usually be observed in the absorption spectrum in the visible and ultraviolet regions, and the objective is the correlation of the maxima with transitions between various electronic states of the molecule. Broad electronic bands sometimes show a fine structure, which may be accentuated at a very low temperature (cf. Fig. 6). Each electronic state can be associated with many vibrational and rotational states, and the fine structure is attributed to vibrational activations. In a complex molecule the energy of the electronic activation may be dissipated in the form of many vibrational activations of much smaller energy. This dissipation and the consequent destruction of structure in the absorption bands are facilitated by loading a molecule with saturated groups, halogen atoms, the nitro group, and other groups capable of vibrations of low energy. Lewis and Calvin have shown the intimate relationship between the fluorescence of organic compounds and the appearance of fine structure in their absorption bands; the prevention of fluorescence and the disappearance of structure are both ascribed to a rapid transfer of the energy of an electronic oscillation to atomic vibrations.

ENERGY LEVELS AND THE ABSORPTION SPECTRA OF MOLECULES

Molecules, like atoms, exist in different electronic states, and spectra arise from transitions between states; but since molecules contain two or more nuclei, they also possess quantized energies of rotation and vibration. Of the two general types of spectra, emission and absorption spectra, the color of organic compounds is concerned with absorption spectra, in which the molecules absorb light and are raised to states of higher energy. The frequency (ν) and the wave length (λ) of the light absorbed are related to the energies E_1 and E_2 of the molecule in the initial and final states by the equation $E_2 - E_1 = h\nu = \frac{hc}{\lambda}$ in which h is Planck's constant and c is the velocity of light. In the consideration of the color of dyes, the primary interest is in absorption in the visible region, although ultraviolet absorption is important for studying the effect of constitutive factors which shift the absorption of organic molecules from the ultraviolet into the visible part of the spectrum, and infrared spectra are being used increasingly to detect the presence of certain groups (e.g., O–H, N–H, C=O, C=N–) in complicated molecules. Among the three types of absorption spectra corresponding to changes in the rotational, vibrational, and electronic states, it is in the transitions between electronic states that the energy differences are of the right magnitude for the absorption of light in the ultraviolet and visible region. Rotational spectra occur in the far infrared, and vibrational (or vibrational-rotational) spectra occur in the near infrared. The energy changes that correspond approximately to absorption at 4,000A. at the violet end of the visible spectrum and to absorption at 8,000A. at the red end are 71 and 35.5 kcal. per mole, respectively. The excitation (photoionization) of the electrons in a single covalent bond requires very large energy and results in absorption in the far ultraviolet (vacuum ultraviolet; Schumann region). The excitation of the mobile electrons in a double bond requires less energy, and ethylene absorbs at about 1,750A. corresponding to an energy increment of about 160 kcal. By increasing the number of double bonds in conjugated positions, or by replacing a C=C bond by such bonds as N=N, the energy increments are made smaller until at about 71 kcal. absorption in the visible region begins.

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[17] See Chapter VII.

[18] Lewis *et al.* *JACS* **65,** 1150 (1943).

[19] For a study of the effect of solvents on the absorption spectra of polymethine dyes see Sheppard *et al.* *ibid.* **64,** 2922 (1942); **66,** 2003 (1944); *Revs. Modern Phys.* **14,** 303 (1942). For a study of the spectral changes of dyes, which do not follow Beer's law, when mixed with colloidal solutions, see Michaelis and Granick, *JACS* **67,** 1212 (1945). See also Canol and Thomas, *J. Chem. Phys.* **17,** 1336 (1949).

In spite of our lack of knowledge of the energy levels of complex molecules such as colored organic compounds and of the impossibility of submitting dye molecules to rigid quantum-mechanical treatment, there has been some success in calculating the spectra of a few conjugated systems characteristic of dye molecules by a combination of the inductive methods of organic chemistry with quantum-mechanical principles.[20-22] The equations of wave mechanics predict "selection rules" which define the "permitted" and "forbidden" transitions between levels. A state can "combine" with another state only if the quantum numbers defining each state bear certain

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[20-22] For recent reviews on color and constitution with special reference to quantum-mechanical aspects, see (20) Maccoll, *Quart. Revs.* **1**, 16 (1947); (21) Symposium on Color and Electronic Structure of Complex Molecules; *Chem. Revs.* **41**, 201–419 (1947); (22) Ferguson, *ibid.* **43**, 385 (1948).

relationships. In the wave-mechanical treatment of electrons as a complex of "standing waves," the quantum states are described by means of the wave functions, and the property of "combination" between states depends on symmetry considerations of the wave functions. "Forbidden" transitions may however become "permitted," with the occurrence of spectra, if the symmetry properties of levels are disturbed by vibrational excitation, collisions, applied electrical fields, etc.

It is only for the hydrogen molecule (consisting of two nuclei and two electrons) and the hydrogen molecule ion (consisting of two nuclei and one electron) that the wave functions can be calculated directly and precisely by solving the Schrödinger wave equation. For all other molecules, methods of approximation have to be used. Two methods of treatment[23–25] have been adopted for organic and especially aromatic molecules. The first is based on the Heitler-London treatment of the hydrogen molecule in which the energy of the system of two nuclei and two electrons is calculated as a function of the distance between the nuclei. When they are brought together, the wave functions combine through resonance, and this coupling by mutual interaction of the two electrons, each of which was originally associated with one proton, is such that the energy of the system differs from the sum of the energies of the two isolated systems. The stability of the binding is increased, and the energy E of the molecule is lower than the energy E_o associated with the electrons moving round their respective nuclei, the difference $(E_o - E)$ being the "resonance energy" or energy of resonance stabilization. A similar (AO—atomic orbital, or valence-bond) treatment is applicable to the two-electron or covalent bond in general and hence is important in organic chemistry.

In the second or molecular orbital (MO; LCAO—linear combination of atomic orbitals; LCAO MO) method, developed by Hückel, Hund, Mulliken, Lennard-Jones, and Coulson, the molecule is constructed mathematically by locating the nuclei (the nuclear charge Z and the charge of the electrons not involved in the transitions which give rise to the spectra) at stated distances from each other, and then adding the outer shell electrons.[26] In the nomenclature of molecular orbital treatment, non-localized or mobile or unsaturation electrons are π-electrons, and the ordinary bonding electrons are σ electrons; the symbols π and σ are also applied to the bonds, a double bond consisting of a σ bond and a π-bond. The benzene molecule, for instance, is considered with the nuclei of the six carbon atoms arranged

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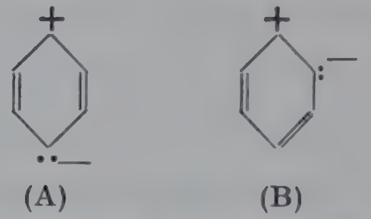
[23-25] For a comparison of these methods, see (23) van Vleck and Shermann, *Revs. Modern Phys.* **7**, 167 (1935); (24) Wheland, *J. Chem. Phys.* **2**, 474 (1934); (25) Bowen, *Annual Repts. Chem. Soc. London* **40**, 12 (1943); see also Longuet-Higgins, *Proc. Phys. Soc. London* **60**, 257 (1948).

[26] For a review of the representation of simple molecules by molecular orbitals, see Coulson, *Quart. Revs.* **1**, 144 (1947).

as a regular hexagon and the electron sextet as a shell round this core; the symmetries and energies of the states of the six electrons are then calculated by wave mechanics. A molecular orbital is the wave function of a single electron in this field of fixed nuclei; electronic interactions are neglected. Each orbital can be occupied by two electrons with opposite spins. Each MO is approximated as a linear combination of atomic orbitals, and the wave function of the molecule is set up as the product of the molecular orbitals. Terms representing the ionic as well as the homopolar states are included: for a diatomic molecule AB, the wave function thus includes terms corresponding to the states $A^+ B^-$, $A^- B^+$, and $A^\circ B^\circ$; and for benzene such structures as (IA) and (IB) are considered. In the interpretation of absorption spectra, the MO method has for this reason advantages over the Heitler-London treatment, which ignores the ionic terms; both methods have severe limitations in their quantitative application to complex molecules such as dyes, and both are now undergoing modifications. The valence-bond treatment, which conforms to the chemical concepts of valence and to the structural pattern of organic chemistry, can be modified to include ionic structures.


(I)

RESONANCE IN ORGANIC CHEMISTRY

Starting with the result of the Heitler-London treatment that covalence is a shared pair of electrons with opposite spin and that the strength of the covalent bond is due to quantum-mechanical resonance, the concept of resonance in its applications to organic chemistry, developed by Pauling and others,[27, 28] has confirmed and extended the electronic interpretations of Robinson, Ingold, and Arndt. If it is possible to assign to a molecule two or more reasonable electronic structures, and if certain other conditions are satisfied, the normal state of the molecule cannot be represented by any of the structures alone, but is compounded of all the structures. The molecule is a " resonance hybrid " of the various structures (or systems of pairing the electrons; " set of canonical structures ") and is more stable (i.e., has lower energy) than any individual structure. The energy stabilizing the molecule is the " resonance energy ".[27, 28a] The main conditions for

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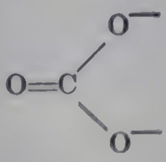
[27] Pauling, The Nature of the Chemical Bond, Cornell Univ. Press, Ithaca, New York, 1940.

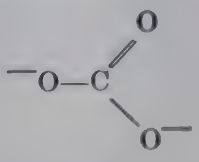
[28] Wheland, The Theory of Resonance, Wiley, New York, 1944.

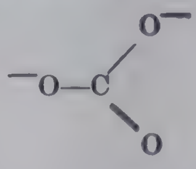
[28a] Kistiakowsky *et al.*, *JACS* **58,** 146 (1936); Bremner and Thomas, *Trans. Faraday Soc.* **44,** 338 (1948).

resonance are that the structures should correspond to the same, or very nearly the same, relative positions of all the atomic nuclei and to the same number of unpaired electrons. The major contributions to the resonance are made by structures of approximately the same stability; structures of lower stability (i.e., higher energy) make correspondingly minor contributions, although these might be important from special points of view such as color and chemical reactivity. The " reasonable " character of a paper structure may be judged in terms of relative stability, which for practical purposes may be roughly computed in the light of such principles as the following: (1) the hydrogen atom is limited to one covalent bond. The " hydrogen bond ",[29] which serves to bridge two electronegative atoms in the same or different molecules, consists of a covalent linkage with one atom and an ionic linkage with a second (donor) atom; it is important in the chemistry of dyes, especially the mordant dyes, and in the affinity of dyes for fibers. (2) The octet rule: carbon, nitrogen, oxygen, and other atoms in the first row of the periodic table are limited to four covalent bonds; structures in which more than eight valence electrons are assigned to one of these atoms can be neglected, and structures in which an atom has a deficiency in the octet are less stable than the structures in which all the eight electrons have been accounted for as bonds or as unshared pairs of electrons. (3) Structures with the largest number of bonds are usually the most stable. (4) As between structures with the same number of bonds, structures in which there are " formal " charges on atoms are relatively unstable, unless the atoms concerned are sufficiently electropositive or electronegative to be capable of forming an ionic bond. The formal charge $F=(n-b-u)$, in which $n=$ the number of valency electrons, b the number of bonds and u the number of unshared electrons. (5) As between two structures in which a negative charge is placed on a more electronegative or less electronegative atom, the former will be more stable.

Examples of resonance structures. The carbonate ion is a resonance hybrid of three equivalent structures, and X-ray analysis[30] of crystalline carbonates has shown that all the three oxygen atoms are equidistant from







the carbon atom and from one another, and lie in a plane with the carbon atom, which is at the center of an equilateral triangle. The X-ray data also establish the important fact that in this symmetrical system each of the three carbon–oxygen bonds has the same length (1.31A.), and is shorter than the average of one double bond and two single bonds between carbon and oxygen. In a nonresonating system the interatomic distance in a C–O bond is 1.43A., and in a C=O bond 1.21A. A shortening of single bond distance and equalization of single and double bond distances are characteristic consequences of resonance.

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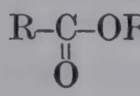
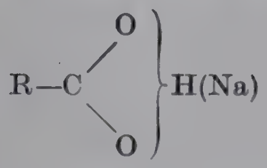
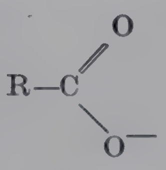
[29] Rodebush, " The Hydrogen Bond " *in* Advances in Nuclear Chemistry and Theoretical Organic Chemistry, Interscience Publishers, New York, 1945; Hunter, *Annual Repts. Chem. Soc. London* **43,** 141 1946).

[30] Elliot, *JACS* **59,** 1380 (1937).

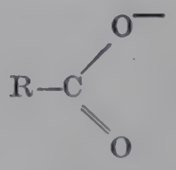
The marked difference in properties between a carboxylic acid and an ester, for instance towards the Grignard reagent, is not obvious from the classical formulation  $R\text{–}\underset{\overset{\|}{O}}{C}\text{–}OR^1$ in which R^1=hydrogen or an alkyl group. Hantzsch observed that esters absorbed more strongly in the ultraviolet than acids and salts, and since absorption of light indicated unsaturation, he concluded that esters were true carbonyl compounds, while acids and salts could be represented as (II). The carboxyl ion is now regarded as a resonance hybrid of the structures (IIA) and (IIB), in which the carbon atom is bound to each of the oxygen atoms by a hybrid shortened link; but the two C–O distances in the undissociated carboxyl group are not quite equivalent. Because of the stability associated with the resonance, a carboxylic acid displays diminished reactivity in reactions involving addition to the C=O group. Another factor in the diminished reactivity of the carbonyl bond in carboxylic acids is hydrogen bonding. Esters also are stabilized by resonance with the structure (III), but this resonance is less significant owing to the energy required for the charge separation, while in a carboxylic acid ionization leads to the equivalent structures (IIA) and (IIB). Increased resonance in an ion is in fact a driving force for ionization, not only in carboxylic acids, but also in phenols and enols.



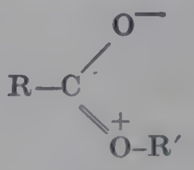
(II)



(II A)

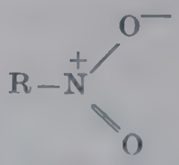


(II B)

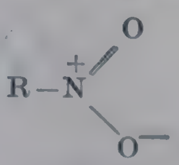


(III)

The two oxygen atoms in the nitro group are equivalent on account of resonance between the structures (IVA) and (IVB) with a possible small contribution from (IVC). In *p*-dinitrobenzene[31] the nitro groups are coplanar with the benzene ring; the two oxygen atoms of the nitro groups



(IV A)



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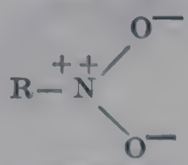

(IV C)

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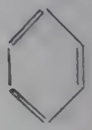
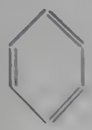
[31] Llewellyn, *JCS* 890 (1947).

are equidistant at 1.23A. from the nitrogen atom, in agreement with the resonance mechanism suggested by Pauling in which the two principal structures are (IVA) and (IVB).

Resonance in the benzene molecule between the two Kekulé structures (VA and B) is complete since they are equivalent and have the same energy; there is in addition the contribution of less stable structures such as (VC), and the molecule is stabilized by the resonance energy of about 41 kcal. The


(V A)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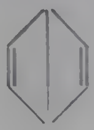
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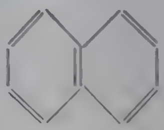
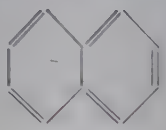
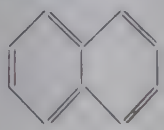
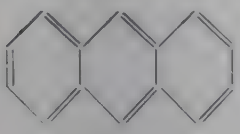
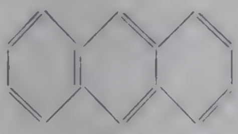

(VI A)

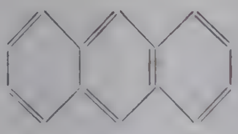

(VI B)

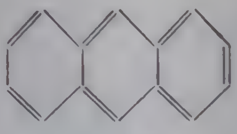

(VI C)

high stability of aromatic ring systems, as well as their optical and other properties, can be ascribed to their character as resonating molecules. The benzene molecule is known from electron and X-ray diffraction studies to be planar; the six carbon atoms lie at the corners of a regular hexagon 1.39A. on edge, whereas the C–C bond distance in ethane is 1.54A., and the C=C bond in ethylene is 1.34A. The main resonance structures for naphthalene, which has a resonance energy of 77 kcal. are (VIA, B, and C). The resonance energy of anthracene is 116 kcal., there being four main contributing structures (VIIA–D).


(VII A)

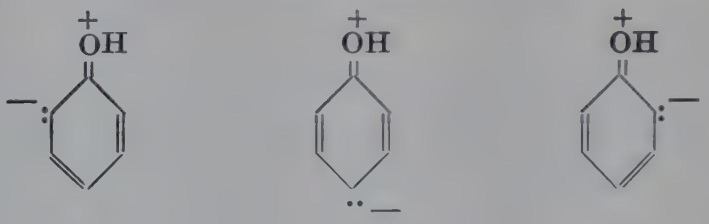

(VII B)

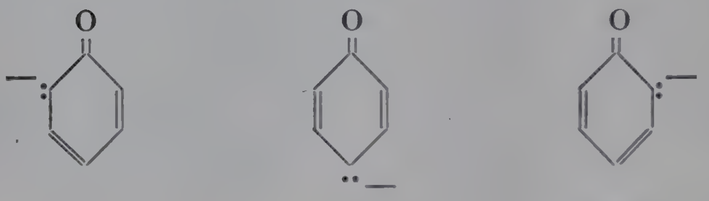

(VII C)


(VII D)

Inductive and resonance effects. The displacement of electric charge is important from the point of view of color and of chemical reactivity, such as substitution in aromatic rings. In addition to the resonance effect (R-effect) which is transmitted through a conjugated path of alternate double and single linkages, there is also an inductive effect (I-effect), which can be transmitted in a saturated chain or may be regarded as a general field effect, and which leads to polarization of the molecule in equilibrium with its environment. Thus, a strongly electronegative atom will tend to pull electrons towards itself. The I-effect will undergo progressively rapid damping with increasing distance from the atom or group producing the effect.

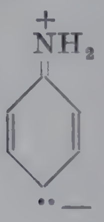
The I- and R-effects of a substituent in an aromatic ring influence the electron distribution at other positions, and therefore the optical and other properties. The R-effect operates in the *o*- and *p*-positions, and it can reinforce or oppose the I-effect, depending on the relative magnitude and direction. These effects are clearly seen in aromatic substitution and in electronic interactions between groups (auxochrome-chromophore effects) in a dye molecule which determine color. In aromatic substitution, the common attacking atoms and groups (e.g., the NO_2, SO_3H, and diazonium groups ; and $:\underset{\cdot\cdot}{\overset{\cdot\cdot}{\mathrm{Cl}}}$, which in a nuclear chlorination seeks to complete its octet, while the second chlorine atom in the chlorine molecule becomes an ion with a complete octet) are electron-seeking (*electrophilic* or *cationoid*) and they are attracted to sites of comparatively high electron density. In phenol, for instance, the structures (VIIIA, B, and C) make a significant contribution to the resonance, and as a result of the increased electron density at the *o-* and *p*-positions, the hydroxyl group in phenol is *o-p-*

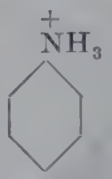

(VIII)

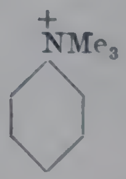

(IX)

(A) (B) (C)

directing. In the phenolate ion, the resonance energy is about 8 kcal. more than that in phenol, on account of the much larger contributions made by the low-energy structures (IX A, B, and C) which do not involve charge separation as in (VIII), and *o-p*-substitution takes place very readily. Aniline behaves similarly to phenol because of similar resonance (e.g., X), but the anilinium ion (XI) (e.g., aniline in presence of a large excess of


(X)

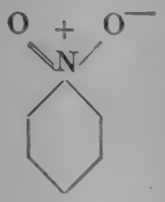

(XI)

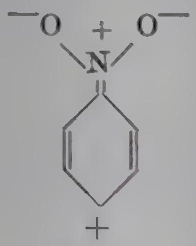

(XII)

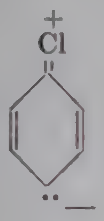
sulfuric acid during sulfonation) behaves very differently from the phenolate ion. The positively charged nitrogen atom in (XI) cannot enter into resonance interaction with the benzene ring, and the inductive effect attracts electrons from the ring. The electron deficiency is felt more in the *o-* and *p*-positions, and in comparison with them the *m*-position is less deactivated, so that substitution takes place in the *m*-position. The phenyltrimethylammonium ion (XII), in which the nitrogen atom carries a much stronger positive charge than in (XI), is more powerfully *m*-directing.

Obviously groups that tend to withdraw electrons will tend to deactivate the ring as a whole with reference to substitution by electrophilic reagents, so that *m*-substitution is much less facile than *o*-*p*-substitution.

In nitrobenzene the main contributors to the resonance are structures such as (XIII), in which the inductive effect of the positively charged nitrogen atom is in the same sense as in (XII); but there are also small contributions from structures such as (XIV) by resonance interaction of the nitro group with the benzene ring, and this effect reinforces the inductive effect. In chlorobenzene the electrophilic inductive effect of the chlorine atom is opposed and overcome by the resonance effect (e.g., XV), so that *o*-*p*-substitution takes place. The contribution of structures such as (XV) to the resonance of chlorobenzene is indicated by the C–Cl bond distance of 1.69A. in comparison with 1.76A. for the unperturbed bond.[32]


(XIII)


(XIV)


(XV)

Groups with mobile electrons which can enter into resonance interaction with the ring or migrate into the ring (e.g., –F, –Cl, $-NH_2$, –OH having unshared pairs of electrons; and unsaturated groups such as –CH=CH– conjugated with the ring) are important in light absorption; in general they produce both bathochromic and hyperchromic effects.

Dipole moments and resonance. Dipole moments are important in the consideration of the color of organic compounds, especially of the intensity of absorption bands. When a substance is placed in an electrical field of unit strength, the total molar polarization (P) measured by the dielectric constant (ε) is the sum of the induced polarization ($P\alpha$) and the polarization ($P\mu$) caused by the polar character of the molecule (i.e., the presence of a permanent dipole in the molecule). These relationships are shown in equation (i), in which M is the molecular weight and d is the density, α the polarizability of the molecule, N the Avogadro number, μ the dipole moment of the molecule, k the molecular gas constant (Boltzmann constant), and T the absolute temperature. The polarizability (α) represents essentially the ease with which electrons (and atoms) in a molecule

$$P=\frac{\epsilon-1}{\epsilon+2}\times\frac{M}{d}=P_{\alpha}+P_{\mu}=\frac{4\pi}{3}N(\alpha+\mu^2/3kT)\;.\;.\;.\;.\;.\quad \text{(i)}$$

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[32] Brockway and Palmer, *JACS* **59**, 2181 (1937).

can be displaced from their normal positions. There are several methods by which the polarizability (α) and the dipole moment (μ) may be separately computed.

Experimental measurement gives the net dipole moment of a molecule, but individual bond moments can be inferred, especially for simple molecules such as water and ammonia. For a diatomic molecule the bond moment is obviously identical with the measured dipole moment. The symmetrical character of molecules such as CCl_4, CO_2, and CS_2 is shown by the absence of a total dipole moment. On the other hand water and hydrogen sulfide have dipole moments; hence the three atoms do not lie in a straight line and the moments of the two dipoles do not cancel one another. The dipole moment of a molecule should normally be the vector sum of the individual bond moments, and any appreciable difference between the observed and calculated dipole moments can be correlated with resonance interactions in the molecule.

In alkyl and aryl chlorides the dipole moment vector is directed along the R–Cl axis, but chlorobenzene has a moment of 1.55 D (D is a Debye unit of 10^{-18} e.s.u.) in comparison with 1.86 for methyl chloride.[33] The lower moment results from the contribution of resonance structures such as (XV); for the same reason the chlorine atom in chlorobenzene is less reactive than that in methyl chloride. In nitrobenzene the inductive and resonance effects (cf. XIII and XIV) operate in the same direction, so that nitrobenzene has a moment of 3.95, which is about 0.64 more than the value for nitroparaffins.

TABLE I

DIPOLE MOMENTS OF SUBSTITUTED BENZENES[34]

	Observed	*Calculated*
C_6H_5-CH_3	0.4	—
C_6H_5-Cl	1.55	—
C_6H_5-NO_2	3.95	—
C_6H_5-NH_2	1.52	—
C_6H_5-OH	1.61	—
p-Cl-C_6H_4-CH_3	1.90	1.95
p-O_2N-C_6H_4-CH_3	4.4	4.35
p-Cl-C_6H_4-NO_2	2.5	2.40
p-O_2N-C_6H_4-NH_2	6.10	5.47
p-O_2N-C_6H_4-OH	5.04	5.56

Benzene has no dipole moment, and the sign of the dipole in a substituted benzene, which represents the direction of displacement of electrons, is indicated by the additivity of the bond or group moments in disubstituted benzenes (Table I). The negative sign of the moment in nitrobenzene follows from the dipole character ($-\overset{+\,-}{\mathrm{NO}_2}$) of the nitro group. By this method atoms and groups can be arranged in a series according to their electronegativity, which may be compared with their influence on the strength of acids and bases.

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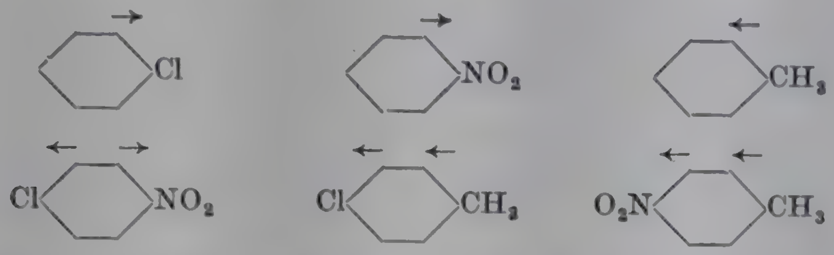
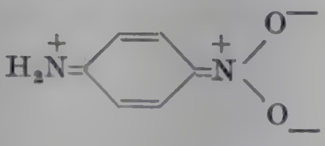
[33] Sutton, *Trans. Faraday Soc.* **30**, 789 (1934).

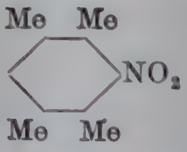
[34] Birtles and Hampson, *JCS* 10 (**1937**); Ingham and Hampson, *ibid.* 981 (**1939**).



When an electron-donor group and an electron-acceptor group are present in *p*-positions, as in *p*-nitroaniline, the dipole moment of the molecule is greater than the sum of the moments of the monosubstituted benzenes as a result of the resonance interaction in structure (XVI). The steric

(XVI)





(XVII)

effect of such resonance produces coplanarity, and conversely, evidence of the steric inhibition of resonance is provided by a decrease in the dipole moment of nitrodurene (XVII), which is 3.39, in the neighbourhood of the value for the nitroparaffins. The *o*-methyl groups prevent coplanar configuration, so that the resonance of the benzene ring with the nitro group is less than that in nitrobenzene.

CHROMOPHORES AND AUXOCHROMES

Saturated molecules ordinarily do not absorb light except in the far ultraviolet, and the action of a chromophore shifts the absorption to lower frequencies. All colored organic compounds are unsaturated in character, and a chromophore may be defined as a group containing one or more multiple bonds. The definition therefore is merely a more precise restatement of Witt's idea of a chromophore. A single chromophoric group, such as the vinylene (–CH=CH–) group, absorbs in the ultraviolet,[35] and to produce visible color two or more chromophores conjugated with each other are necessary. Further, unsaturation in dye molecules is usually associated with oxygen and nitrogen atoms in a manner which enables ready reversal of the linkages in the conjugate chain, so that dye molecules are resonance hybrids. It then becomes necessary to speak of a chromophoric system or systems in a dye molecule, rather than single chromophores.

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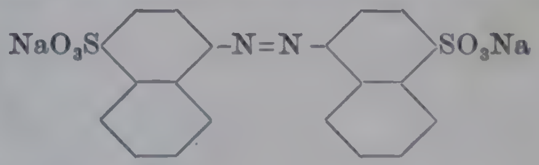
[35] For a review of data on ultraviolet absorption and its correlation with molecular structure, see Braude, *Annual Repts. Chem. Soc. London* **42,** 105 (1945).

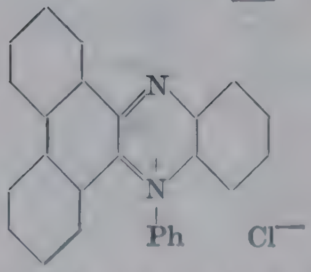
Color may be deepened and intensified progressively by the multiplication of chromophores and by the replacement of weaker by stronger chromophores, as explained later.

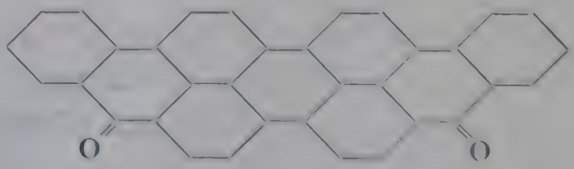
Auxochromes are more difficult to define than chromophores, and there has been some confusion regarding the nature and function of auxochromes. It will be recalled that Witt employed the term for groups, such as hydroxyl and amino, which were "weakly salt-forming" and imparted dyeing properties to a colored substance and which also intensified the action of the chromophore. These two effects are distinct and separate, and need to be considered separately. In the sense of salt-forming groups auxochromes have one function. With the exception of methods in which an insoluble dye is applied to textiles as a pigment incorporated in a resin binder, dyes are applied to textile fibers from an aqueous medium; a dye molecule therefore must contain a group which will render it soluble in water (under neutral, acidic, or alkaline conditions), directly or after suitable chemical treatment such as reduction with hydrosulfite-alkali or sodium sulfide. Dyes therefore contain salt-forming groups, or groups which can be converted before dyeing into salt-forming groups. Examples of the former are Witt's auxochromes, to which must be added sulfonic, carboxyl, quaternary ammonium groups, etc., which have the function of enabling a colored compound to be applied as a dye and whose influence on the color of the molecule may be variochromic (cf. Wizinger's positive and negative auxochromes). Two dyes of interest in this connection, as dyes not containing auxochromes in the Witt sense, are 1,1′-azonaphthalene-4,4′-disulfonic acid (XVIII) which dyes wool orange, and Flavinduline (XIX) which is a basic dye for tannin-mordanted cotton. Dyes of a second type, which contain no auxochrome in the original solid state and in which auxochromes are introduced during the process of solubilization prior to dyeing, are exemplified by the vat dyes. Dibenzanthrone (XX)



(XVIII)

(XIX)





(XX)

is an intense blue dye which does not contain an auxochrome; on treatment with hydrosulfite-alkali it is reduced to a dihydro compound, which has two phenolic hydroxyl groups functioning as auxochromes.

Auxiliary groups, which are not "salt-forming" and which therefore do not fall within the category of Witt's auxochromes, may be introduced in dye molecules for the purpose of increasing the affinity for textile fibers, or "substantivity." In this sense they may also be included among auxochromes. An example is the amide (–CO–NH–) group. The phenomenon of substantivity for textile fibers and theories of dyeing are however discussed in Chapter XLI, although they are in some ways associated with the problem of color, and it is found that bathochromic and hyperchromic effects, especially the latter, sometimes run parallel to increasing substantivity.

From the standpoint of the color of organic compounds an auxochrome is best defined as a substituent atom or group which *increases* the *intensity* (ε) of the absorption of light due to a chromophore. An auxochrome may also shift the main absorption band (λmax) to longer wave length, just as a second chromophore conjugated with the first increases the intensity of absorption in addition to shifting it to longer wave length. There are, however, adequate reasons for associating chromophores with a bathochromic effect and auxochromes with a hyperchromic effect as invariable effects, which may or may not be accompanied by a hyperchromic effect in the first case and a bathochromic effect in the second.

A given auxochrome may increase the intensity of absorption only for certain chromophores, and only when it is situated in a suitable position with reference to the chromophore; the same substituent may decrease the absorption for other chromophores. An "auxochromic effect" has thus more significance than an "auxochrome," since an atom or group functions as an auxochrome only under certain conditions. For this reason the effect of auxochromes and chromophores must be considered in conjunction with each other, and Brooker[36] has made the acceptable suggestion of a composite term, *auxochromophoric system*, to express the combination of auxochromes and chromophores.

The distinction between an auxochrome[37] and a chromophore in light absorption is one of degree, rather than of kind, since auxochromes with the exception of alkyl groups and chlorine atoms, which have unique features and are discussed separately, produce high intensity absorption in the ultraviolet. Nevertheless, it is convenient to distinguish between auxochromes and chromophores on the basis of the electron distribution in the two types of groups, and of the specific effect of auxochromes, as now suggested, of increasing the intensity of absorption. While chromophores are groups containing multiple bonds and in general are electron-attracting, auxochromes are singly bound atoms or groups with unshared pairs of electrons. In an auxochromophoric system therefore, electron mobility and the absorption of light result from the electronic interaction between auxochromes and chromophores by which the contribution of highly conjugated and polarized structures to the resonance of the molecule is increased.

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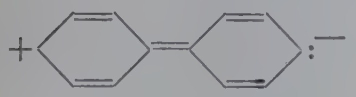
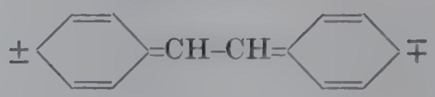
[36] "Resonance and Organic Chemistry" *in* Advances in Nuclear Chemistry and Theoretical Organic Chemistry, Interscience Publishers, New York, 1945.

[37] For a discussion of auxochromic properties in relation to the position of the substituent element in the periodic system, see Bowden, Braude, and Jones, *JCS* **948** (**1946**).

Diphenyl has 100 times the intensity of absorption of benzene, and the powerful auxochromic effect of one phenyl group on the other is due to resonance interaction, as a result of which the contribution of ionic structures such as (XXI) is greatly increased.


(XXI)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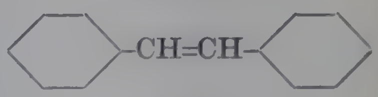

(XXIII)

For stilbene resonance structures such as (XXII), which are associated with the absorption of light, may be considered as contributing to the normal

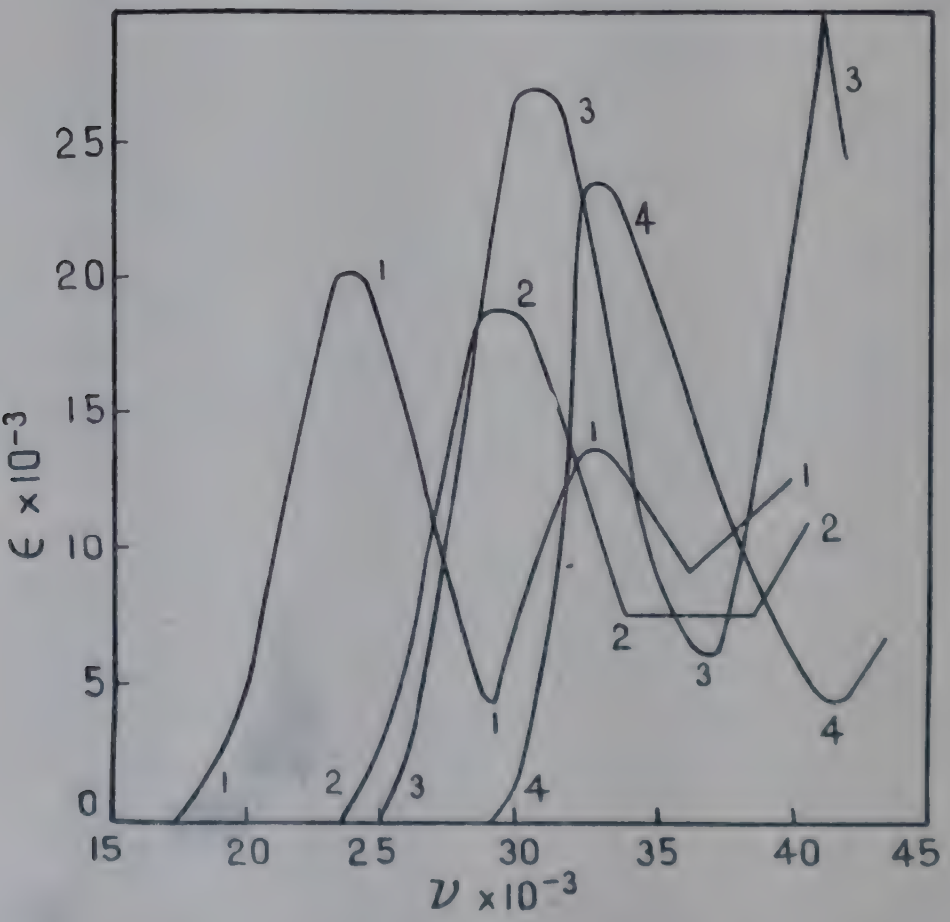
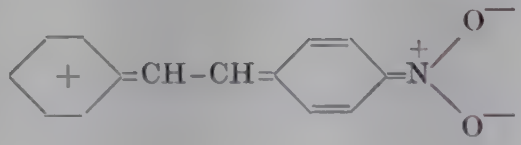
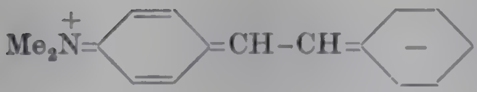
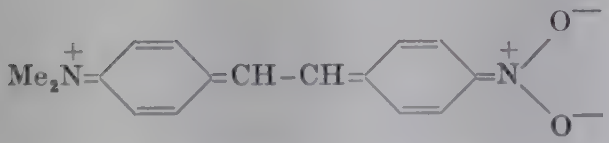


Fig. 3. Absorption curves of four stilbenes in alcohol: (1) *p*-nitro-*p*′-dimethylaminostilbene; (2) *p*-nitrostilbene; (3) *p*-dimethylaminostilbene; and (4) stilbene (Hertel and Luhrmann).

state of the molecule (XXIII), but because of the high energy of charge separation, only to a small extent; the interatomic distance (1.44A.) by the X-ray method indicates about 18% double bond character for the bonds between the benzene rings and the aliphatic carbon atoms. The contribution of structures such as (XXII) may be increased by the introduction of an electrophilic or an electron-donor group at one end of the molecule, so that the energy of the structure may be lowered by providing an atom or atoms which can carry a negative or positive charge more readily than carbon.[37a] The absorption curves[38] of stilbene and of three *p*-substituted stilbenes are given in Fig. 3. In *p*-nitrostilbene (XXIV) the bathochromic effect is produced by an additional chromophore, the nitro group; and in *p*-dimethylaminostilbene (XXV) a similar effect is produced by an auxochrome, the dimethylamino group. The shift in absorption towards lower frequency is almost identical in the two cases, but the intensity of absorption, as postulated earlier, is increased by the introduction of the auxochrome, while the nitro chromophore has a hypochromic effect. In 4-nitro-4′-dimethylaminostilbene (XXVI) the bathochromic effect is more


(XXIV)


(XXV)


(XXVI)

pronounced than that in (XXIV) and (XXV), and is greater than the sum of the effects of the nitro and the dimethylamino groups; on account of the electron-attracting character of the two oxygen atoms and the electron-donor character of the two nitrogen atoms, the structure (XXVI) makes a large contribution to the optically important resonance of the molecule. These resonance effects influencing light absorption are analogous to those discussed earlier in connection with dipole moments.

Similar effects are apparent from the absorption spectra of *p*-hydroxyazobenzene, *p*-nitroazobenzene, 4-nitro-4′-hydroxyazobenzene, and the last substance in alkaline solution. While for the reasons explained in the case of the stilbene derivative (XXVI), 4-nitro-4′-hydroxyazobenzene (XXVII) is deeper in color than the hydroxy compound, the same substance in alkaline solution exhibits a large bathochromic shift. In the resonance structures

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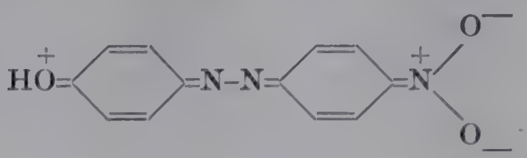
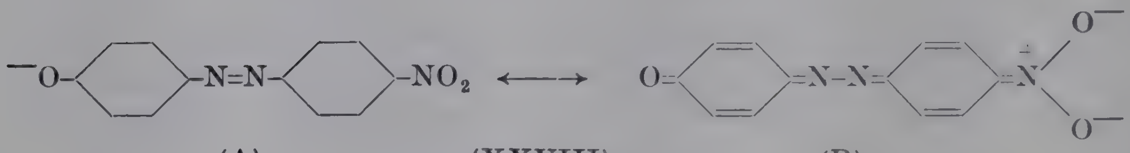
[37a] For a study of charge distribution and bond orders in aminostilbene and related molecules, see Coulson and Jacobs, *JCS* 1983 (**1949**).

[38] Hertel and Lührmann, *Z. physik. Chem.* **44,** 261 (1939).



(XXVII)



(A) (XXVIII) (B)

(XXVIIIA and B) for the ion, only the movement of a charge is involved and the low energy of the transition is responsible for the deeper color in comparison with that of the undissociated compound (XXVII).

The influence of alkyl groups on light absorption. The absorption curves of acetone and of hexaethylacetone (Fig. 4) clearly demonstrate the influence of alkyl groups in increasing both the intensity and the wave length

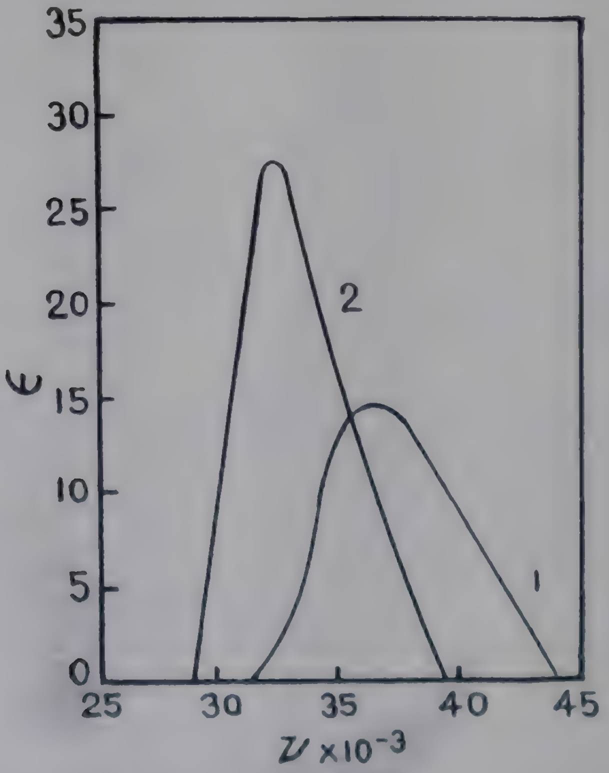


Fig. 4. Absorption curves of (1) acetone and (2) hexaethylacetone in hexane (Lewis and Calvin).

of absorption. The first absorption band of benzene (λmax 2,560A.; ε_{max} 250) is shifted to λmax 2,620A. and ε_{max} 300 in toluene. Lewis and Calvin[9] explain the effect as due to induction, which they regard as a perturbation in existing electronic paths without alteration of their essential character. Auxochromes with unshared electron pairs provide, through resonance, new electronic paths.

The ability of alkyl substituents in a chromophoric system to increase absorption is in line with their *o*-*p*-directing power as nuclear substituents in the benzene ring. A methyl group in the benzene ring increases the electron density in the *o*- and *p*-positions, and the effect is particularly marked in mesitylene, which can couple with diazotized 2,4-dinitroaniline. Toluene has a dipole moment (0.4 D), the methyl group being positive with reference to the phenyl, and it has been suggested that hyperconjugation,[28, 39] may be responsible for the effect. Hyperconjugation is an electronic interaction occurring with covalently saturated groups, especially a methyl group, postulated in substances such as propylene to explain the fact that the heat of hydrogenation of an olefin is decreased by the presence of alkyl substituents on the unsaturated carbon atoms; and it may be pictured as

$$\underset{(A)}{H_3C{-}CH{=}CH_2} \longleftrightarrow \underset{(B)}{\overset{+}{H}\ \ CH_2{=}CH{-}\overset{-}{\ddot{C}}H_2}$$

a resonance effect occurring in propylene between the normal structure (A) and the less stable structure (B).

When the size of the alkyl group is increased from methyl to ethyl, etc., the bathochromic shift becomes progressively less. This has been shown in the case of the *n*-alkylbenzenes (toluene to *n*-hexylbenzene); the vibrational fine structure of the benzene spectrum disappears in the higher members.[40] *tert*-Butylbenzene is brominated about 115 times faster than benzene at 25°;[41] spectroscopic evidence also indicates the hyperconjugation of the *tert*-butyl group, which however is less than that of the *primary* and *secondary*-butyl groups.[42] Price has studied the effect of alkyl substitution on the absorption spectra and ionization potentials of many classes of molecules, and has shown that it is mainly due to preferential stabilization of the ionic or excited state, largely as a result of hyperconjugation and charge transfer.[43] The bathochromic effect of a methyl group is stronger in 1- than in 2-methylnaphthalene;[44] in a given molecule the proportion of conjugation or hyperconjugation of a substituent is greater the more highly charged the position at which it is attached, and bathochromic effect varies proportionally with this index of conjugation.

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[9] See p. 326.

[28] See p. 334.

[39] Deasy, *Chem. Revs.* **36**, 146 (1945); Mulliken, Rieke, and Brown, *JACS* **63**, 41 (1941); Bateman and Koch, *JCS* 600 (**1944**); 216 (**1945**); Baker and Nathan, *ibid.* 1844 (**1935**). See also Crawford, *Quart. Revs.* **3**, 226 (1949).

[40] Pestemer and Gübitz, *Monatsh.* **64**, 426 (1934).

[41] Berliner and Bondhus, *JACS* **70**, 854 (1948).

[42] Matsen, Robertson, and Chuoke, *Chem. Revs.* **41**, 273 (1947).

[43] Price, *ibid.* **41**, 257 (1947).

[44] Pullman, *Compt. rend.* **224**, 1354 (1947).

Chlorine as an auxochrome. The simple C–Cl and C–Br linkages exhibit very little absorption in the region of the spectrum above 2,000A.

The unshared electrons of the chlorine atom enable small, but significant, contributions to be made by such polar structures as (XV); since however this has to overcome the negative inductive effect, chlorine is usually a very feeble auxochrome.[45] Thus the spectra of 2-chlorophenanthrene and phenanthrene are so similar that structures involving a double bond between the halogen atom and the ring can make no significant contribution to the activated state of the molecule.[46] On account of the size of the atom, chlorine in the *o*-position to a chromophore (e.g., in an azo dye) is capable of a steric inhibition of resonance with a consequent decrease in absorption.

Electrons as Quantized Oscillators

Lewis and Calvin[9] in 1939 formulated a comprehensive theory of the color of organic compounds, in which it was assumed that electrons in a molecule acted as oscillators subject to the simple rules of quantization; that the absorption of light was due to the excitation of electronic oscillations whose extremes were represented by certain polar resonance structures; and that the types of oscillations were indicated by the resonance structures contributing to the ground and excited states of the molecules. The Lewis-Calvin treatment brought order into a mass of data, and has been of value in the correlation of the light-absorption characteristics of certain classes of dyes with their chemical constitution, although applications of quantum-mechanical methods to problems of molecular structure and spectra have shown the inadequacy of the Lewis-Calvin theory in its quantitative aspects.

The absorption curves of ethane, cyclohexane, ethylene, butadiene, and cyclopentadiene are given in Fig. 5. For ethane two polar structures (IA) and (IB) may be written in addition to the normal structure; their contribution to the actual state of the molecule is small, and it is the

$$\text{(I)}\qquad \underset{\text{(A)}}{H_3\overset{+}{C}\ \ \overset{-}{C}H_3}\qquad\qquad \underset{\text{(B)}}{H_3\overset{-}{C}\ \ \overset{+}{C}H_3}$$

polarizability of the bond or bonds in a molecule which is associated with the absorption of light. The two lowest curves in Fig. 5 are characteristic of saturated systems; electrons in single bonds are not affected by wave lengths greater than about 2,000A. In the curve for cyclohexane there is a shift towards lower frequency because of the Baeyer strain in the ring. The curve for ethylene is characteristic of a simple double bond, in which resonance occurs to a considerable degree. In the transition between electronic states resulting in light absorption, the ground and excited states are resonance hybrids of the structures (II A, B, and C) and of less stable structures which are left out of account; the ground state is represented essentially by (A), while (B) and (C) make large contributions to the two

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[45] See also Hamer and Matsen, *JACS* **70**, 2482 (1948).

[46] Jones, *ibid.* **67**, 2143 (1945).

[9] See p. 326.

(II) $H_2C{=}CH_2$ $H_2\overset{+}{C}{-}\overset{-}{C}H_2$ $H_2\overset{-}{C}{-}\overset{+}{C}H_2$

(A) (B) (C)

excited states which arise from resonance. Butadiene absorbs at lower frequency than ethylene, and the two upper curves in Fig. 5 are characteristic

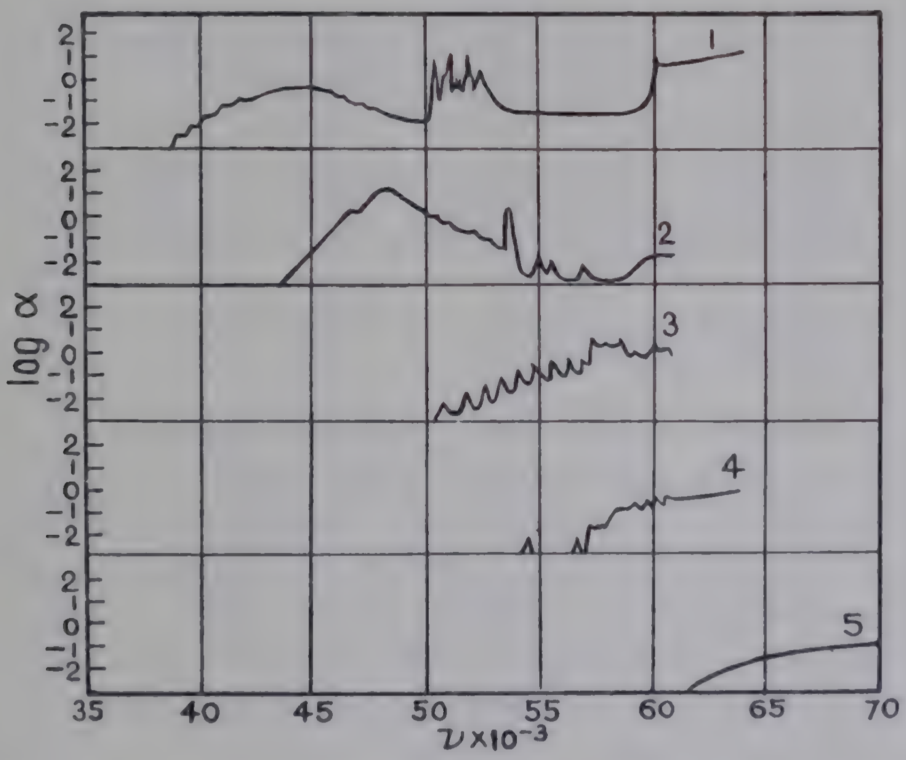

Fig. 5. Absorption curves of (1) cyclopentadiene; (2) 1,3-butadiene; (3) ethylene; (4) cyclohexane; and (5) ethane (Lewis and Calvin).

of conjugated systems. The resonance stabilization of the excited state in butadiene is greater than that in ethylene because of contributions from a number of structures such as (III A and B) which do not differ widely in energy. In the spectrum of butadiene and of cyclopentadiene there is a new wide band, which is not present in ethylene; this is regarded as a "fundamental band" which indicates that each double bond has lost its individuality as an oscillator, the conjugated system having become subject to certain rules governing the whole molecule. With increased conjugation in the system there is a displacement of the fundamental band of absorption to longer wave lengths.

(III) $\overset{+}{C}H_2—\overset{-}{C}H—CH=CH_2$ (A) $\overset{+}{C}H_2—CH=CH—\overset{-}{C}H_2$ (B)

The polarizability of the double bond in ethylene is associated with its chromophoric character, and other double-bonded structures in which there is an increased strain may be expected to absorb at lower frequencies or function as "stronger" chromophores than an ethylenic compound.[47] Taking C=N, C=O, N=N and C=S as examples of other types of double bonds, the first absorption maxima of stilbene and of a series of its analogs are compared in Table II.

TABLE II

Compound	*First absorption*	*Visible color*
	A.	
Stilbene Ph–CH=CH–Ph	2950	None
Benzalaniline Ph–CH=N–Ph	3300	None
Benzophenone Ph–$\underset{\underset{O}{\Vert}}{C}$–Ph	3300	None
Azobenzene Ph–N=N–Ph	4500	Orange
Thiobenzophenone Ph–$\underset{\underset{S}{\Vert}}{C}$–Ph	6200	Blue

It is one of the postulates of the Lewis-Calvin theory that "every displacement from the ideal state makes further displacement easier," i.e., increases the mobility of electrons.[48] The fact that *p*-nitroaniline has a considerably greater dipole moment than the sum of the moments of nitrobenzene and aniline is an illustration of the principle, and the large contribution from the structure (IV), which is responsible for the moment and the increase in electron mobility, is also responsible for a marked increase in light absorption.

The similar dyes (VI) and (V) have λmax 3,920A. and 5,060A. and have dipole moments 4.06 D and 7.68 D, respectively.[49]

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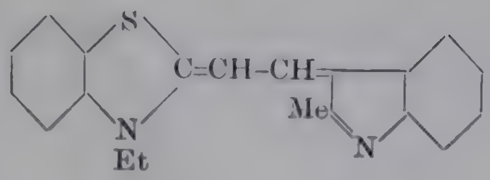
[47] See, however, Hertel, *Z. Elektrochem.* **47,** 28 (1941).

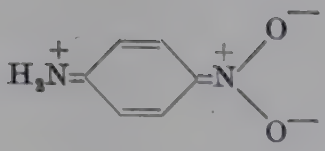
[48] For a discussion of the chromophoric powers of the systems dianil, diene, and azine, which decrease in the order named, see Ferguson and Goodwin, *JACS* **71,** 633 (1949).

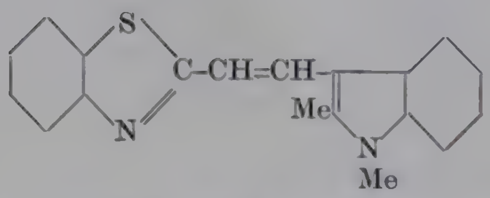
[49] Brooker *et al.*, *ibid.* **62,** 1116 (1940); see also Kushner and Smyth, *ibid.* **71,** 1401 (1949).



(V)

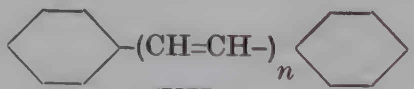
(IV)





(VI)

Nearly linear oscillators. For molecules which may be considered to be nearly linear so far as electronic oscillations associated with light absorption are concerned and in which there is an unbroken chain of alternate single and double bonds, it is possible to derive empirical relationships between the length of the conjugate chain and the frequency of



(VII)

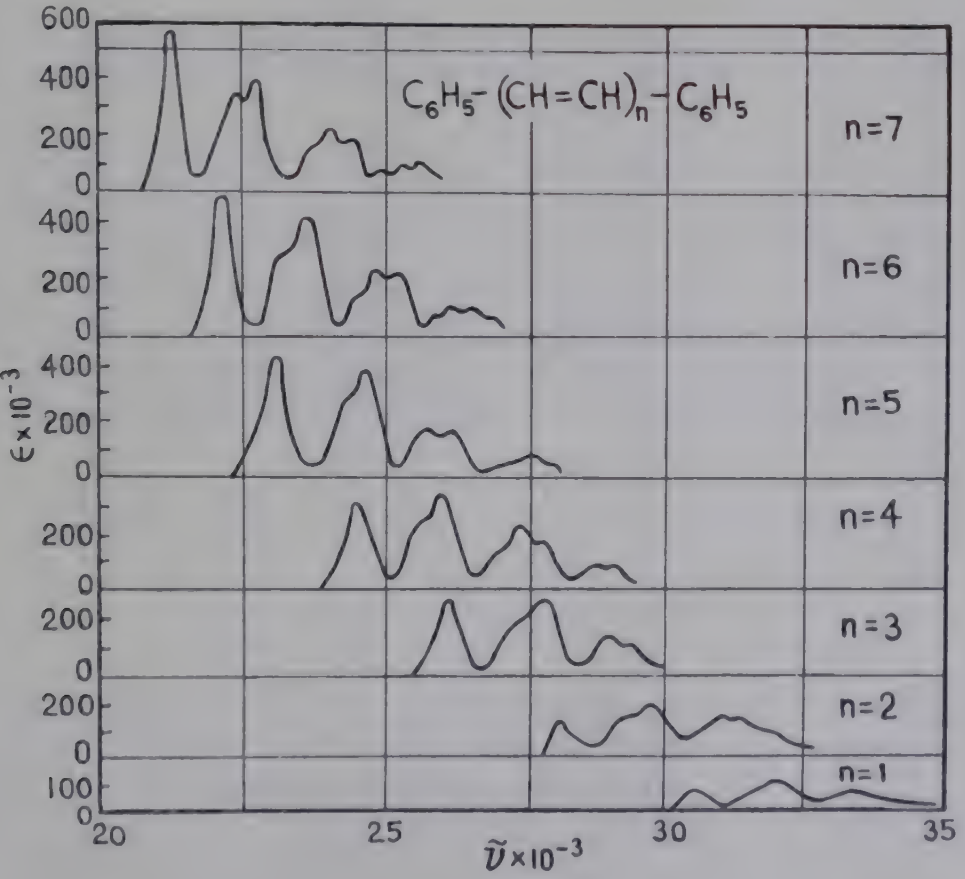


Fig. 6. Absorption curves in the visible and near ultraviolet of diphenylpolyenes in ether-alcohol mixture at —196°.

absorption. Three main types of such linear oscillators have been investigated. In the simplest type, the diphenylpolyenes (VII), it has been shown[50] that there is a steady decrease in the frequencies of the absorption bands with increase in n (Fig. 6); and when the frequencies of the first maxima are plotted against n (adding an arbitrary "color equivalent" of 1.5 double bonds for each of the end phenyl groups or adding the actual number of double bonds in the end groups of series such as the carboxylic acids), all the points approximate to the same curve (Fig. 7) for about 70 compounds. The sharp definition and structure in the curves in Fig. 6, ascribed by Hausser and Kuhn to the atomic vibrations characteristic of the olefins, were obtained in a solution of ether and alcohol at —196°.

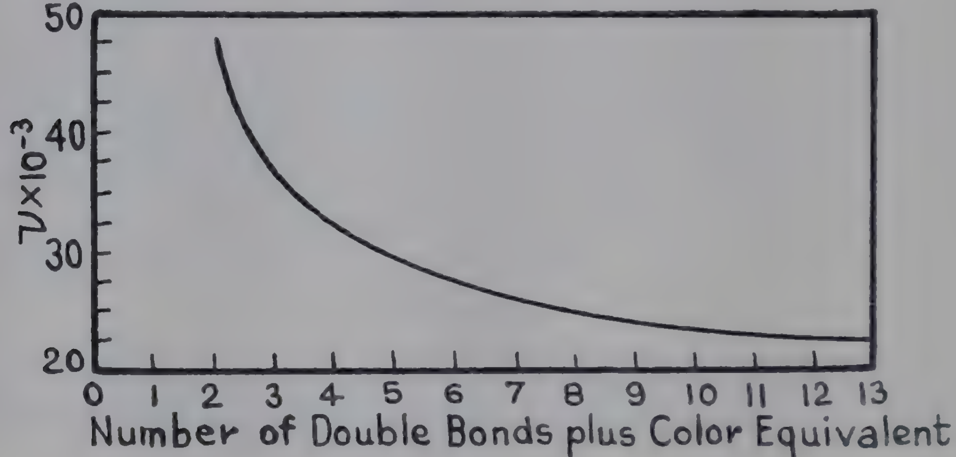
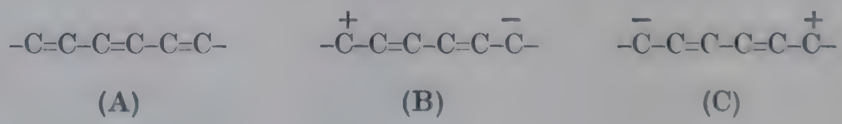


Fig. 7. Plot of frequency of first maximum against the total number of conjugated double bonds for 70 compounds of the polyenic type.[50]

Omitting the terminal groups, the polyene chain (VIII) may be represented by the structure (A) and by polar structures such as (B) and (C), which represent the extreme or limiting structures. A chain of n conjugated double bonds may be considered as a single linear oscillator



$$-C{=}C{-}C{=}C{-}C{=}C- \qquad -\overset{+}{C}{-}C{=}C{-}C{=}C{-}\overset{-}{C}- \qquad -\overset{-}{C}{-}C{=}C{-}C{=}C{-}\overset{+}{C}-$$

(A) (B) (C)

(VIII)

or as a system of n unit oscillators moving exactly in phase; it is simpler to do the latter. The fundamental frequency ν (the frequency of the light which can change the oscillator from quantum number 0 to 1) is given by the expression (i), in which k is the coefficient of restoring force and m the mass of the effective electrons in each unit; k is a constant for the oscillator which is related to the polarizability α by the equation $k=e^2/\alpha$. When the system of n unit oscillators is now replaced by a single oscillator of force

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[50] Hausser, Kuhn, *et al.*, *Z. tech. Physik.* **15,** 10 (1934); *Z. physik. Chem.* **B29,** 363 (1935).

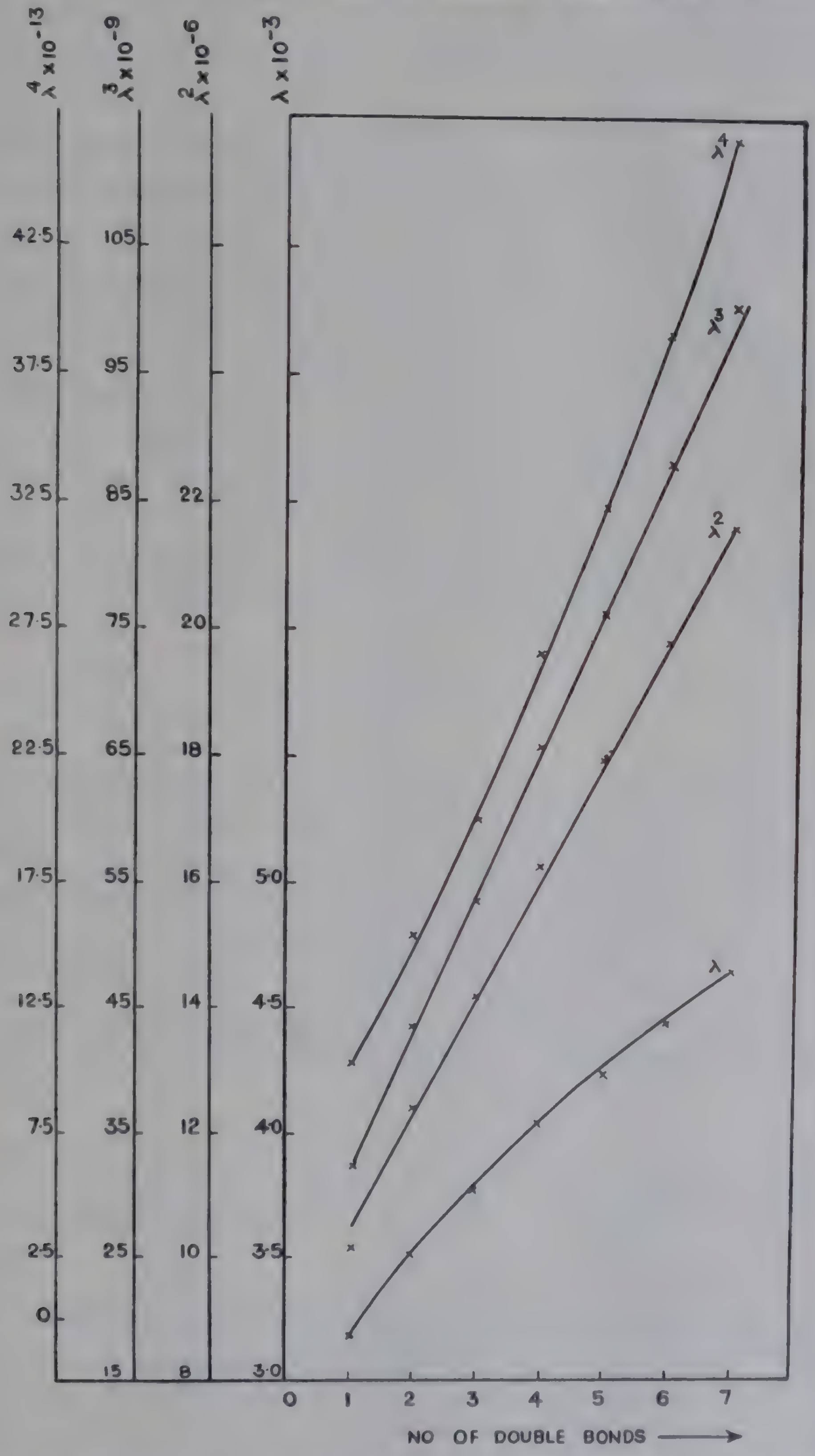


Fig. 8. Plot of the number of units of the polyenic chain in diphenylpolyenes against λ (the wave length in A. of the first absorption band), λ^2, λ^3 and λ^4.

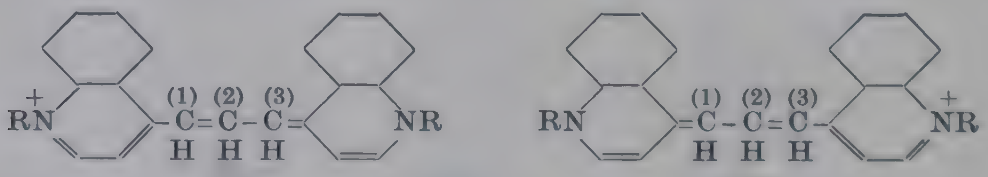
constant k, the total mass of the effective electrons is nm, and the characteristic frequency ν for the series of molecules (VII) is given by the expression (ii) which is merely equation (i) with m replaced by nm. The wave lengths of

$$\nu=\frac{1}{2\pi}\sqrt{k/m} \; . \, . \quad \text{(i)} \qquad \nu=\frac{1}{2\pi}\sqrt{k/nm} \; . \, . \quad \text{(ii)} \qquad \lambda=\frac{2\pi c}{\sqrt{k/nm}} \; . \, . \quad \text{(iii)}$$

the first absorption maxima are then given by equation (iii), and if all the constants are replaced by a new constant k^1, we have the equation $\lambda^2=k^1n$. Figure 8, in which λ^2 is plotted against n from the data in Fig. 6, indicates the linear relationship for the diphenylpolyenes; the intercept of the line on the n-axis shows that, if λ^2 is made not merely linear with n but proportional to it, each phenyl group is equivalent to 2.35 double bonds. Brooker[51] has pointed out that actually the function is remarkably insensitive to the power of λ; for λ^3 plotted against n the curve is still a straight line, and using λ^4 a definite curvature is apparent, but in the reverse direction to that of the curve of n against λ.[52] Kuhn[52a] regards the polyene chain as a series of coupled linear oscillators, each oscillator corresponding to a double bond of the conjugated system, and he obtains the expression (iv).

$$\lambda_1=\frac{1.57\cdot10^3}{\sqrt{1-0.922\cos\frac{\pi}{n+1}}} \qquad \text{(iv)}$$

Considering that the main contributor to the resonance states of the polyenes (VIII) is the classical structure (A), Lewis and Calvin assumed that even in the excited states the electrons never get far from the positions indicated in this structure, and the restoring force within a single unit is not appreciably affected by the electrons of the next unit. The ion of a cyanine such as (IX) represents a different type of oscillator. Instead of one main contributing structure, there are two equivalent low-energy structures (A and B) which contribute equally to the resonance. Lewis and Calvin then assumed that the electron distribution between the carbon atoms 1 and 2, and 2 and 3, is the same, which would be true if we take an average of the extreme structures only. If the electronic cloud is diffuse



(A) (B) (IX)

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[51] Private communication.

[52] See also Anslow, *J. Applied Phys.* **16**, 41 (1945); Compton and Bergmann, *J. Org. Chem.* **12**, 363 (1947).

[52a] *Helv. Chim. Acta* **31**, 1780 (1948).

and more or less uniformly distributed throughout the length of the chain, the restoring force is dependent mainly on the position of the neighboring electrons, and the oscillation is analogous to the longitudinal vibrations in an elastic string, where the frequency is inversely proportional to the length of the string. For cyanine ions of the general type (IX), the wave lengths of the first absorption maxima should therefore be expected to increase linearly with the number of double bonds between the two nitrogen atoms. Hamer's data[53] for a series of carbocyanines are plotted in Fig. 9.

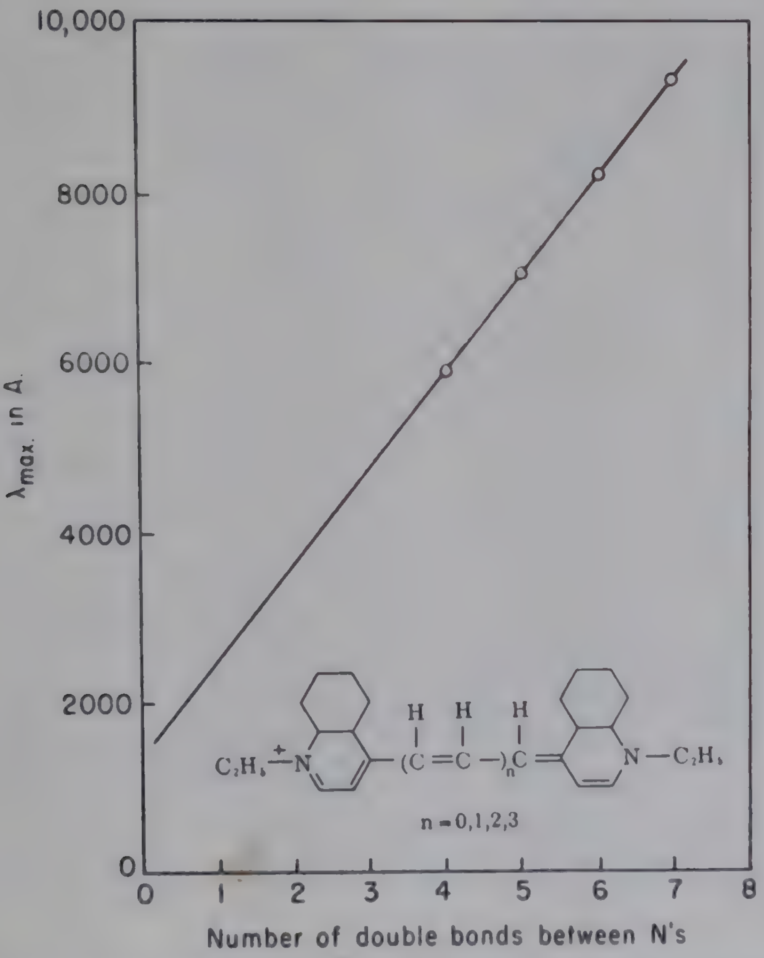

Fig. 9. Plot of the wave length of the first absorption band against the number of double bonds between the nitrogen atoms for a series of carbocyanines.

Quantitative relationships between the structures and spectra of numerous symmetrical and unsymmetrical polymethine dyes have been deduced by Brooker.[54] Vinylenic homologous series of other types (e.g., diphenylpolyeneazines) have also been investigated in the derivation of empirical equations defining the influence of structure on absorption.[55]

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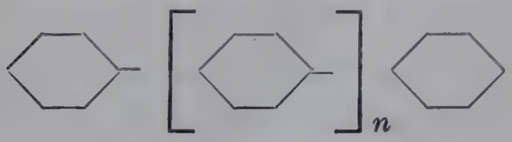
[53] Hamer *et al.*, *Proc. Roy. Soc. London* **A154**, 703 (1936); **A163**, 138 (1937).

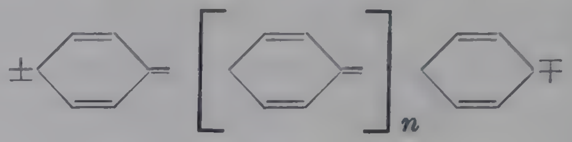
[54] See later.

[55] Cf. Ferguson and Branch, *JACS* **66**, 1475 (1944).

Lewis and Calvin cite the polyphenyls (X) as a third type of approximately linear oscillator. The weak absorption of benzene is associated with the large contribution of the Kekule structures; in derivatives of benzene and other cyclic resonators the absorption increases with an increase in the contribution of ionic structures. Structures such as (XI) for the polyphenyls, which determine the light absorption, can only contribute at the expense of the Kekulé resonance. When n is small, the percentage increase in length due to an additional phenylene group produces so great an increase in the polarizability that it counteracts the Kekulé resonance, and there is a marked increase in the wave length of the first absorption maximum. When n is large the importance of these two conflicting effects is in the reverse order; an additional phenylene group produces so small an increase in the polarizability that it is unable to overcome the Kekulé resonance of the added group. Because of this difference between the character of the polyphenyls as linear oscillators and of the diphenylpolyenes, k also increases with n in equation (iii), and it is to be expected that in the polyphenyls the increase in λmax with increase in n will become progressively smaller. For a series of p-polyphenyls, Gillam and Hey[56] have found that λmax varies as follows: diphenyl 2,515; triphenyl 2,800; tetraphenyl 3,000; pentaphenyl 3,100; hexaphenyl 3,175A.

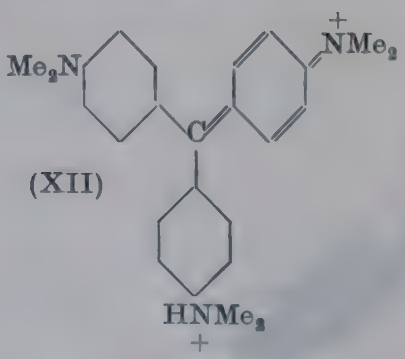


(X)

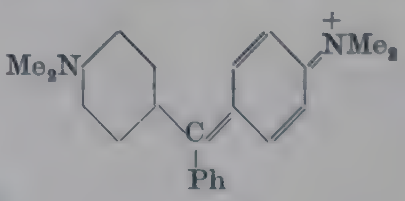


(XI)

Acid-base indicators. Some of the first applications of the recognition of the ions of dyes such as the triphenylmethanes as resonance hybrids have been in correlating their behavior as indicators for acids and alkalis with the effect of the hydrogen or hydroxyl ions on the resonance structures. Adams and Rosenstein[11] examined the color changes of Crystal Violet in acid solution, and showed that the absorption spectra corresponded to successive additions of protons to the cation. Thus the ion of Crystal



(XII)



(XIII)

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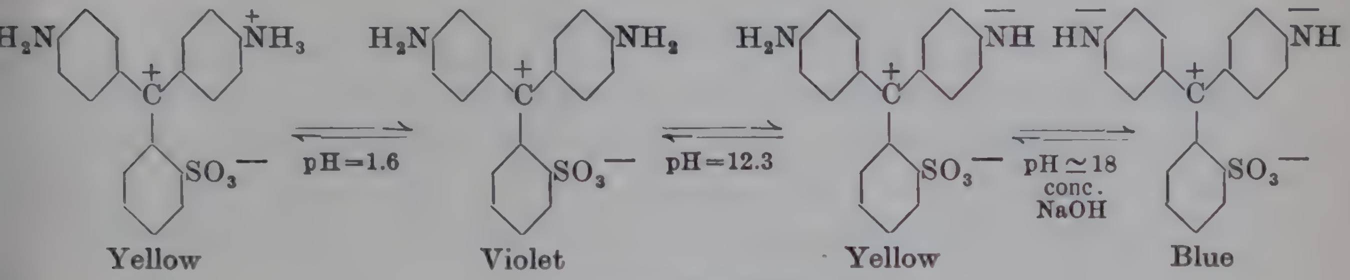
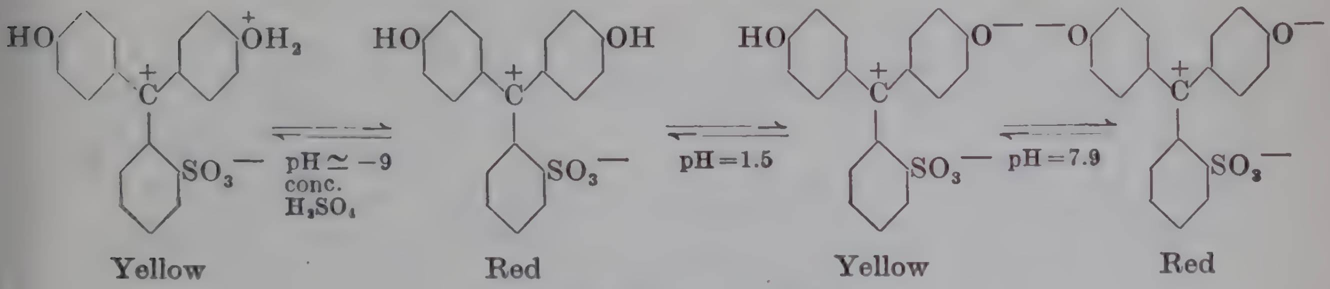
[56] *JCS* 1170 (1939).

[11] See p. 327.

Violet in acid solution, when one proton is added as in (XII) to an NMe_2 group, which can therefore no longer participate in the resonance, has an absorption spectrum very similar to that of the cation of Malachite Green, for which one of the extreme resonance structures is shown in (XIII). Schwarzenbach[57] has explained in this manner the color changes of many indicators. Examples are Anilinesulfonephthalein and Phenolsulfonephthalein.

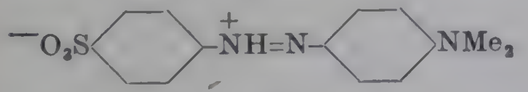


Anilinesulfonephthalein

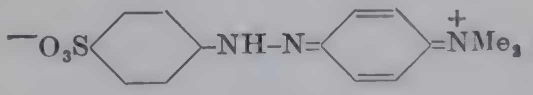


Phenolsulfonephthalein

Methyl Orange in alkaline solution is yellow, being in the azo form.[58] On the addition of acid (pH below 3.1), the color deepens to red; an azo nitrogen atom takes on a proton, and the zwitterion (XIV) is then a resonance hybrid of the structures (A) and (B).



(A)



(B)

(XIV)

Schwarzenbach[59] has proposed a theory of color, based on color changes at varying pH and other properties of dyes. In passing through a pH range of −10 to +17 using solvents other than water, there is usually a periodic change of color. In the case of dyes with two auxochromic groups, a bathochromic change of color always follows a hypsochromic one, and vice versa. The larger the number of auxochromic groups, the more complicated is the periodicity. The position of the long wave absorption band is decided by the symmetry of the colored particle, which affects the resonance energies of the various limiting structures. It is also affected by the length of the resonance chain between the auxochromic groups, and by specific effects due to the constitution and nature of these groups. The resonance energies of the majority of colored particles can be estimated from acidity constants.

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[57] Schwarzenbach *et al.*, *Helv. Chim. Acta* **20**, 490, 498, 627, 654, 1591 (1937).

[58] For a discussion of the several forms of Methyl Red in connection with their reactivity in the photooxidation of phenylhydrazine, see Livingston and Pariser, *JACS* **70**, 1510 (1948).

[59] *Z. Elektrochem.* **47**, 40 (1941).

INSULATING GROUPS

When two or more chromophoric systems are present in a molecule, the effect is roughly additive if the systems are separated by two or more single bonds, i.e., by saturated groups such as $-CH_2-$ and $-CH_2-CH_2-$, which break the conjugation and act as insulators between the two electronic oscillators. This important principle[60] is illustrated in Fig. 10. Dyes (II) and (III) absorb at nearly the same frequency, and the intensity of absorption (ε) of the dye (II) is about twice that of (III). The dye (I) in which the conjugation is unbroken acts as a single oscillator, and it absorbs at a lower frequency than (II) and (III). The spectrum of 6,15-dihydrohexacene (IV) is nearly the same as the sum of the spectra of naphthalene and anthracene.[61] Diphenyl ether, *p*-diphenoxybenzene, and 4,4′-diphenoxy-

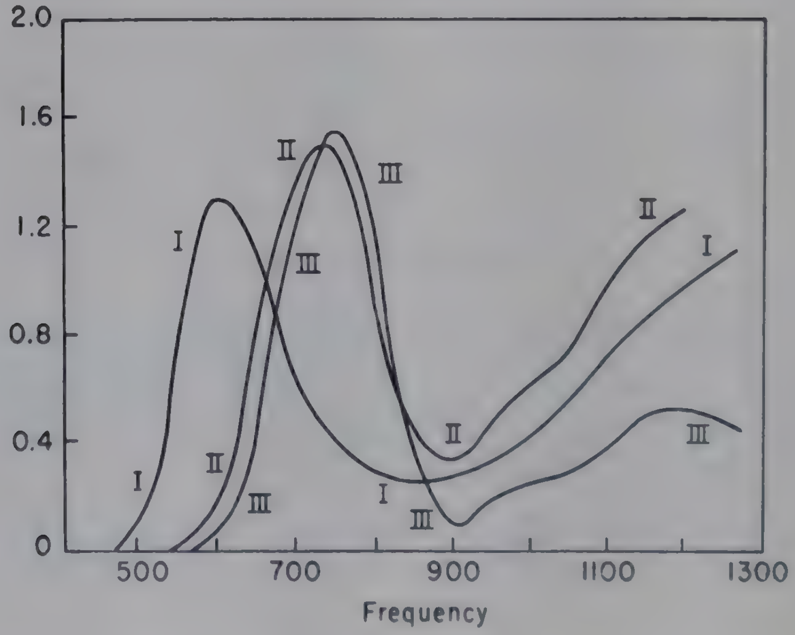

Fig. 10. Absorption curves of some azo dyes in alcohol.

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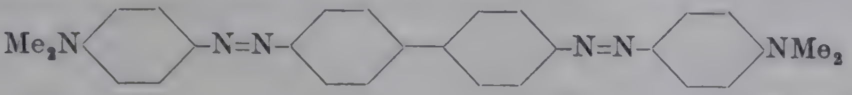
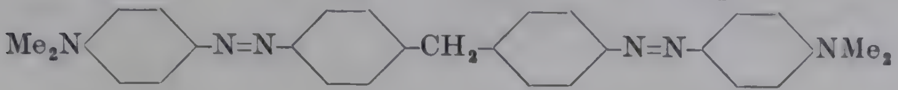
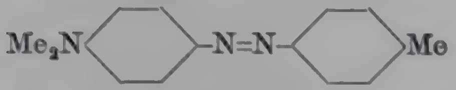
[60] Piper and Brode, *JACS* **57**, 135 (1935).
[61] Clar, *Ber.* **75**, 1283 (1942).

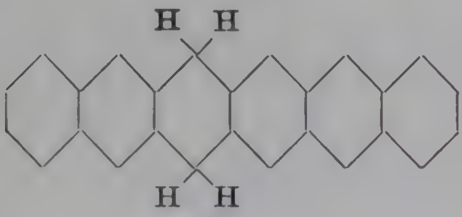
diphenyl ether have similar spectra.[62] The NH group is to some extent a barrier to bathochromic effect, but there is a hyperchromic effect due to increased weight of polar structures.[63] The benzene ring is a chromophoric block if the substitution is *meta*; thus both benzalaniline and (V) absorb at about the same wave length (λmax 2,630A. and 2,670A.; $\varepsilon_{\max}$ 16,800 and 33,800 respectively).[55]

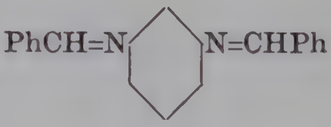

(I)


(II)


(2× ε)

(III)


(IV)


(V)

The union of two or more dye units, by methods other than conjugation which results in a single chromophoric system, is of very great value for modification of shades by internal compensation in the dye molecule. In dyeing and printing, a self-shade (i.e., a shade produced from a single dye) has advantages over a shade obtained by using a mixture of two or more dyes. Many examples of the preparation of high-molecular dyes by linking up smaller dye molecules by means of phosgene, cyanuric chloride, etc., are quoted in later chapters, and it will be useful to have further data on the relative insulating effects of groups such as –O–, –CO–, –NH–, –S–, $-SO_2-$, –NH–CO–NH–, –CO–NH–, *m*-phenylene, the triazine ring, etc. It is important to remember in this connection that the effect of the insulation between chromophoric units is dependent on the character of the chromophores as well as on that of the intervening group. If the chromophoric units which are linked together are highly mobile systems, some electronic interaction can occur even when the two units are not conjugated with each other.[64] In a compound having two unconjugated chromophores the light absorption approximates more nearly to a simple summation the wider the separation between the chromophores in the molecule.[65]

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[62] Mayer-Pitsch, *Z. Elektrochem.* **49,** 368 (1943).

[63] Izmail'skii and Simonov, *J. Gen. Chem. U.S.S.R.* **16,** 1659 (1946).

[55] See p. 355.

[64] See also Braude, *JCS* 1902 (**1949**); Kumler, Strait, and Alpen, *JACS* **72,** 1463 (1950); Ramart-Lucas and Guilmart, *Compt. rend.* **229,** 1336 (1949).

[65] Ramart-Lucas, *Bull. soc. chim. France* **51,** 289 (1932).

Bands of "partial oscillations." In addition to a fundamental absorption band at lower frequency, a conjugated system may sometimes show a "partial band" (a weak localized band) due to one of the chromophores.[9, 66] An example is diacetyl (curve 1 in Fig. 11) which shows a resolved, fundamental band at about 4,200A. in the visible region, as well as a "partial" band not far from the band for acetone (curve 3; $\varepsilon \times 2$)

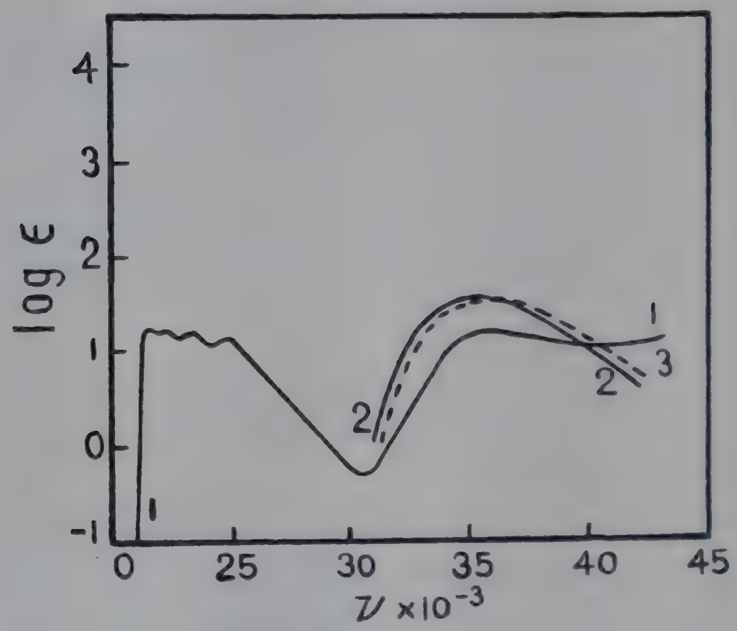

Fig. 11. Effect of insulation of carbonyl groups on the absorption: (1) $CH_3COCOCH_3$; (2) $C_2H_5COCH_2CH_2COC_2H_5$; (3) CH_3COCH_3 (2ϵ). Solvent hexane.

associated with an isolated carbonyl group.[67] Curve 2 in Fig. 11 is for dipropionylethane, which is almost identical with curve 3 representing twice the absorption coefficient of acetone, and which is another example of the effect of an insulating group, discussed earlier.

The identification of a "partial" band in a conjugated system, which is due to the specific effect of a powerful chromophore, corresponds to the older interpretations of absorption spectra which assigned characteristic frequencies to the presence of particular groups. The appearance of such a partial band does not depend on the insulation of the chromophoric group concerned from the rest of the molecule, which would prevent a fundamental oscillation through the molecule as a whole. Absorption

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[9] See p. 326.

[66] Kortüm, *Z. Elektrochem.* **47,** 55 (1941).

[67] For a study of the absorption spectra of various types of α,β-unsaturated ketones, see Woodward, *JACS* **64,** 76 (1942); Gillam *et al.*, *JCS* 486 (**1942**); 432 (**1945**); Wilds *et al.*, *JACS* **69,** 1985 (1947).

bands in the ultraviolet are in general characteristic of individual chromophores, and absorption in the visible region is associated with conjugated systems acting as single oscillators.

The absorption curves of three cyanine dyes, studied by Brooker and Smith,[68] are shown in Fig. 12. The formulae of the dye ions (VI, VII and VIII), only one of the resonance structures being shown in each case, indicate that (VIII) may be regarded as a composite of (VI) and (VII).

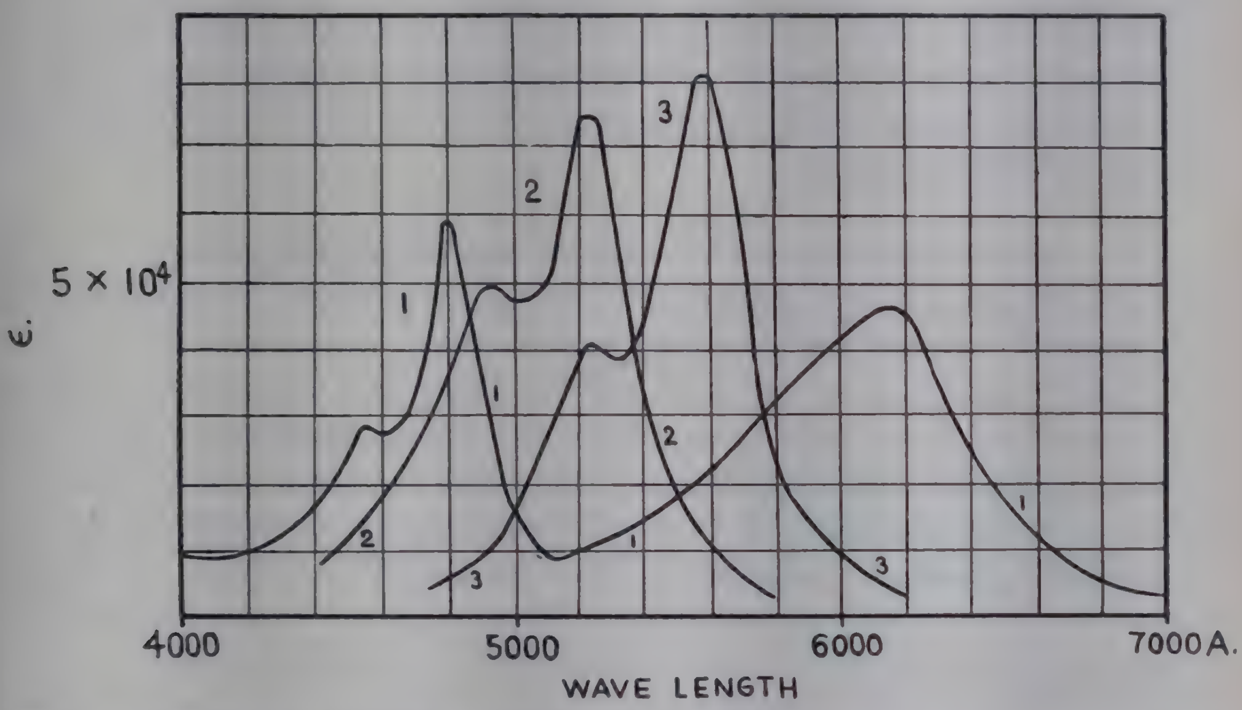
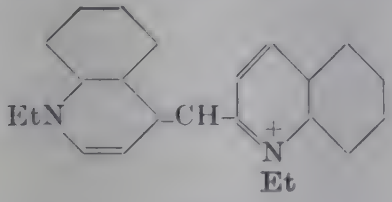
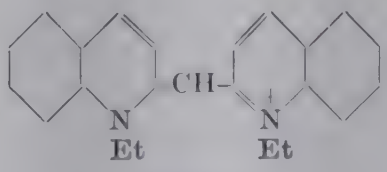


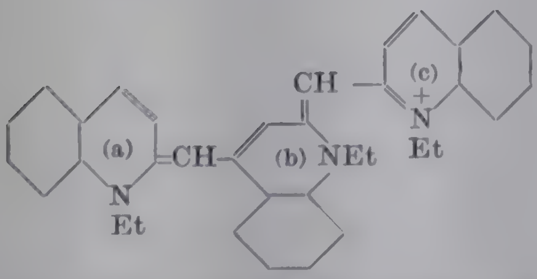
Fig. 12. Absorption curves of three cyanines in alcohol: (1) (VIII); (2) (VII); (3) (VI).



(VI)



(VII)



(VIII)

The ion (VIII) has three nitrogen atoms capable of carrying a positive charge; with the charge on nitrogen atom (a) or (c), an oscillation through the whole molecule can be pictured, and this fundamental absorption may be justifiably associated with the low frequency band at about 6,250A. in curve 3 representing (VIII). The high frequency band in curve 3 is obviously similar to the maxima in curves 1 and 2 for the ions (VI) and (VII) and represents a band of partial oscillation, corresponding to an oscillation in that part of the ion (VIII) which is similar to the ion (VI) or (VII), or to a merging of the two. The hypsochromic shift in the partial band for (VIII) is to be ascribed to the cross conjugation in (VIII), as a result of which neither of the oscillations corresponding to those in (VI) or (VII) can be completely effective.

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[68] *Ibid.* **59**, 67 (1937).

LIGHT ABSORPTION AND THE GEOMETRY OF MOLECULES

In the " nearly linear oscillators," such as the polyenes, the polyphenyls and some of the cyanines, the large polarizability responsible for color in the visible region is along one axis, and the major or x axis will be more or less along the line of maximum extension; but in Malachite Green and other compounds in which the conjugated system extends in two dimensions, we are no longer dealing with even approximately linear oscillators. Two fundamental bands corresponding to the two axes of oscillation can sometimes be identified (x and y bands). When a planar molecule does not possess a center of symmetry, x and y bands are to be anticipated, but the location of the y band in the spectrum may be difficult on account of great differences in the intensities of the two bands, if the polarizability or electron mobility in one direction is much larger than in the other.

For a few relatively simple and approximately linear molecules (p-azoxyanisole,[69] diphenyloctatetraene and diphenyldodecahexaene[9]) for which X-ray data have indicated the relative positions of the atoms in the crystals and hence the direction of the axis of the molecule, it has been found by examining the absorption of polarized light that the absorption is at a maximum when the electric vector of the polarized light is roughly along the axis of the molecule.

A molecule having a high degree of polarizability in three directions can exhibit three fundamental bands (x, y, and z bands) associated with the three axes, but only a few examples are available in which z bands have been characterized. Confusion is likely to arise between the names x, y, and z for the three possible axes of polarization in a molecule and similar names which are sometimes ascribed to the long wave, medium wave, and short wave absorption bands in the molecular spectrum. Since polarization along the length of the molecule, as in anthracene cited later, need not correspond to the long wave absorption band, the names x, y, and z are used in the present treatment to represent the three axes of polarization and the *corresponding* bands; from the point of view of their wave lengths, the absorption bands are referred to as first, second, and third bands in the order of decreasing wave length. The x and y axes represent respectively the length and width of the molecule, and z an axis perpendicular to the molecular plane. The assignment of absorption bands to the axes of polarization in a molecule has generally to be made on the basis of indirect and circumstantial evidence; but proof of the y band has been obtained for a few substances (e.g., Malachite Green) by two methods.[70] The first depends on the production of oriented molecules in a rigid solvent, and the second on the use of polarized fluorescence. For 1,1′-diethyl-2,2′-cyanine chloride (I), Scheibe[71] has been able to characterize x, y, and z bands, and to relate them to the structure and orientation of

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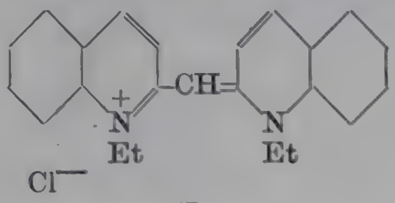
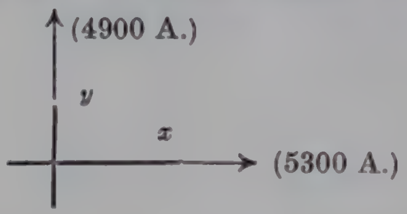
[69] Bernal and Crowfoot, *Trans. Faraday Soc.* **29**, 1032 (1933).

[9] See p. 326.



(I)



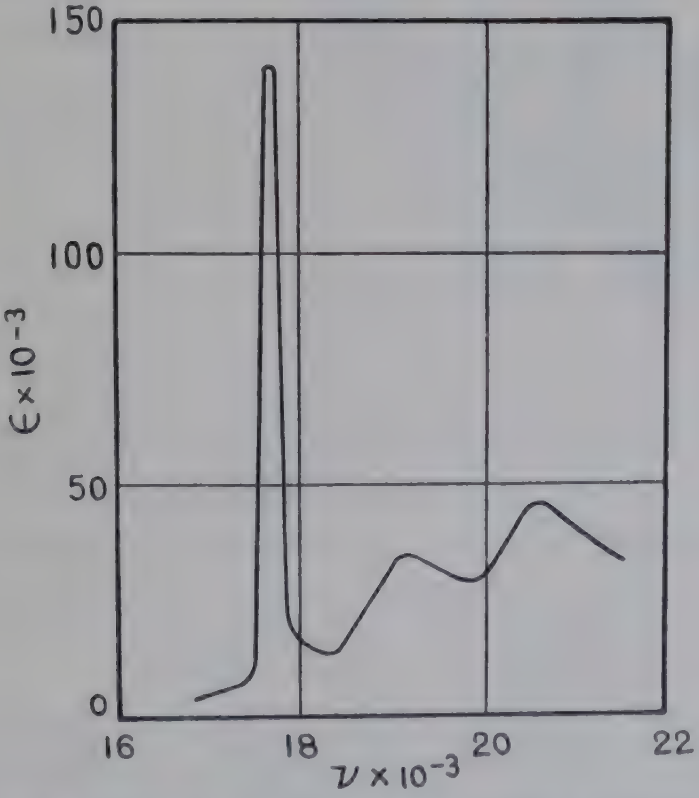


Fig. 13. Fluorescence band of 1,1′-diethyl-2,2′-cyanine chloride (0.01*M* in water at 20°).

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[70] Lewis and Bigeleisen, *JACS* **65,** 2102 (1943).

[71] *Angew. Chem.* **52,** 631 (1939); see also Jelley, *Nature* **139,** 631 (1937).

the molecules. In very dilute aqueous solution, the dye shows an x band at 5,300A. and a y band at 4,900A., but when more concentrated solutions are examined, in which the dye forms a fibrillar colloid, a new narrow and very intense band appears at about 5,700A. (Fig. 13). This is a z band, which arises from absorption along the length of the long threads of polymerized molecules formed by the flat molecules lying face to face. There is an intermolecular electronic interaction between the flat molecules which are stacked together in a pile in the threads and this interaction, polarized linearly along the threads, is responsible for the new band. Figure 14 illustrates the arrangement of the molecules of (I) responsible for three-dimensional polarization and the appearance of the x, y, and z bands. The formation of colored molecular complexes by aromatic compounds is apparently associated with this face to face alignment of the flat molecules and an intermolecular resonance. The transfer of excitation energy by resonance from molecule to molecule in organic crystals has been shown in the anthracene-naphthalene and other systems by measuring the fluorescence when excited by visible or ultraviolet light.[72]

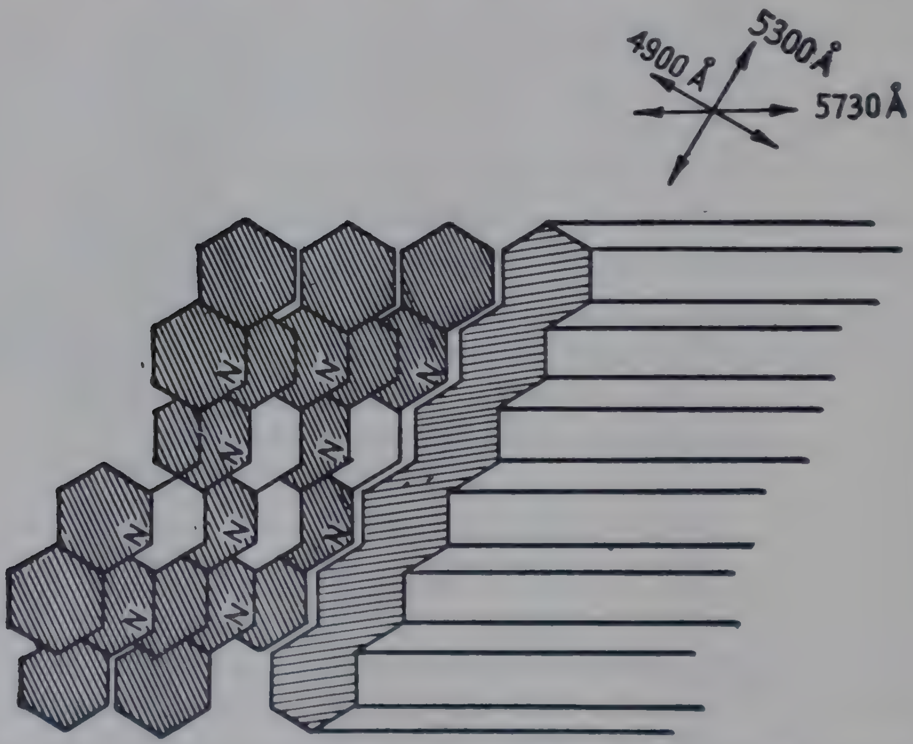


Fig. 14. Absorption and structure of the polymer of 1,1′-diethyl-2,2′-cyanine chloride.[71a]

The part played by the π-electrons in the long wave length spectra has been shown in hexamethylbenzene,[73] which is a planar molecule. The absorption spectrum has been determined by using polarized light with the electric vector respectively parallel and perpendicular to the plane of the molecule, and the extinction is about a tenth under the latter condition.

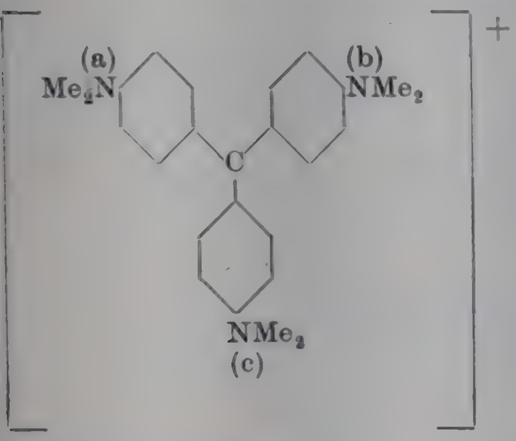
[71a] Reproduced by permission of Prentice-Hall, Inc., from *The Theory of Organic Chemistry* by Branch and Calvin (1941).

[72] Bowen *et al.*, *Proc. Phys. Soc. London* **62A,** 26 (1948).

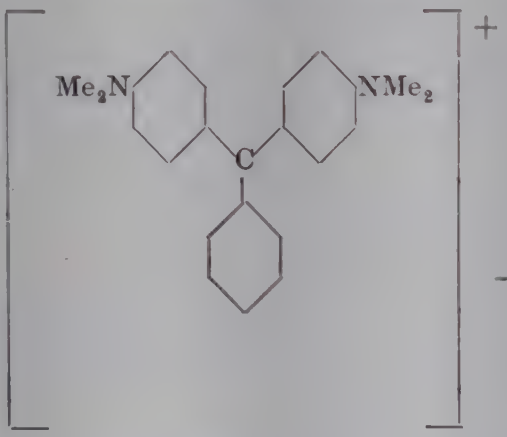
[73] Scheibe, St. Hartwig and Müller, *Z. Elektrochem.* **49,** 372 (1943).

The long wave absorption at 4,950A. in Fluorescein corresponds to light polarized in the molecular plane and along the line of greatest width of the molecule, and is therefore the x band; the emitted green fluorescence is also polarized along the same line. The ultraviolet absorption band at 3,125A. of the Fluorescein ion corresponds to light absorption polarized along the short axis of the molecule (the y band); but light absorption by this band emits the same green fluorescence, so that the y oscillation excited by the absorption polarized along the short axis is partly converted into the x oscillation, the energy of which then emits the green fluorescence.[70]

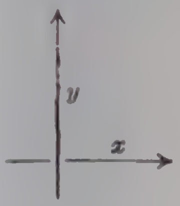
In the ion of Crystal Violet (II) which has a center of symmetry,[74] polarizability is the same in all directions of the plane, so that the x and y bands coincide (λmax 5,900A.). Malachite Green (III) on the other hand is unsymmetrical and there are two well-defined bands in the visible region (6,250 and 4,230A.; Fig. 15; curve 3). The x direction may be reasonably assigned as the direction of oscillation between the N atoms, and the y direction as the one involving the unsubstituted phenyl group. If the polarization in the y direction in Malachite Green is increased by introducing a methoxyl or methyl group in the third phenyl group, the y band is shifted to lower frequency, while the x band undergoes a slight shift in the opposite direction (Fig. 15; curves 1 and 2). Curve 4 in Fig. 15 represents the ion of Michler's hydrol (IV) in which the unsubstituted phenyl group

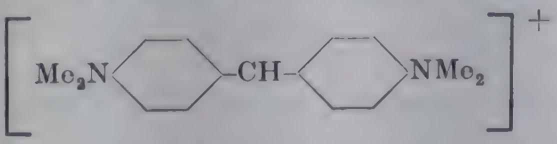


(II)
Crystal Violet ion



(III)
Malachite Green ion





(IV)

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[70] See p. 363.

[74] This would not be true of the B-isomer of Crystal Violet found by Lewis, Magel, and Lipkin, *JACS* **64**, 1774 (1942).

of Malachite Green is replaced by a hydrogen; the scope of oscillation in the y direction is greatly limited and the second band has become a very weak band in the ultraviolet.[70]

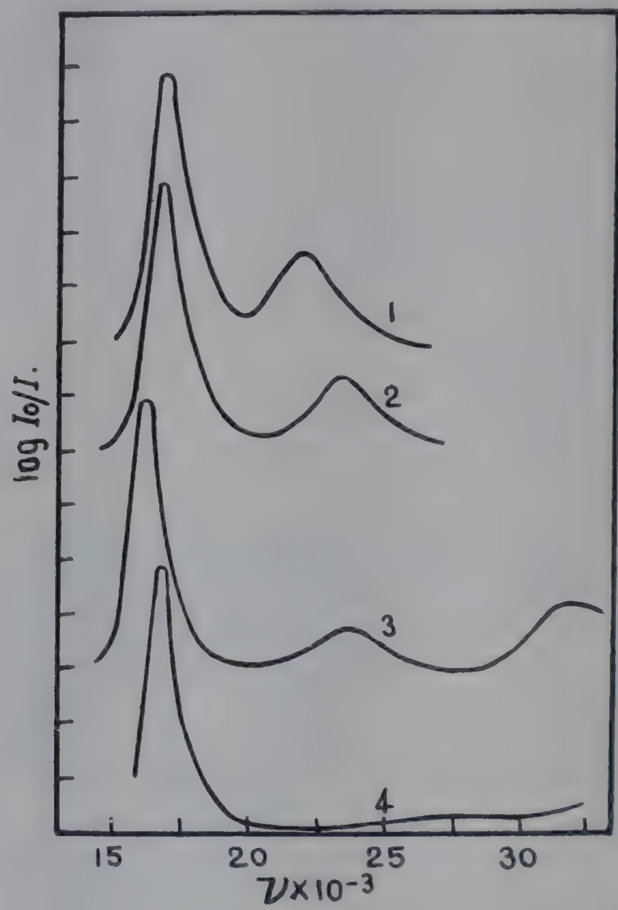

Fig. 15. Bands x and y of (1) p-methoxy-Malachite Green; (2) p-methyl-Malachite Green; (3) Malachite Green (identical with curve for Acid Green); (4) the ion of Michler's hydrol. (1), (2) and (3) in ethanol; (4) in glacial acetic acid.

When the color of a substance is associated with a charge transfer along a certain path in the molecule, the frequency of absorption will be increased by any influence which diminishes the effective charge, and the frequency will be decreased by any influence which increases this charge. This effect explains the deeper color of Malachite Green (λmax 6,230A.) in comparison with that of Crystal Violet (λmax 5,900A.), which was inexplicable in terms of the older theories of color, since the latter dye has an extra auxochrome. The resonance which is associated with the color is more effective in the Malachite Green ion (III). If it is assumed that the fundamental band is due to electronic oscillation in one direction, the phase in the oscillations of the Crystal Violet ion (II) in which the positive charge is on the nitrogen atom (c) will not contribute to the oscillations between (a) and (b). It may be stated roughly that two-thirds of a positive charge will be available for the uniaxial oscillation associated with the fundamental band of Crystal Violet, while a whole charge will be available for the corresponding oscillation in Malachite Green; hence the deeper color of the latter. The bathochromic change in passing from Crystal Violet to Methyl Green can be explained similarly. In the Methyl Green ion (V), as in the Malachite Green ion (III), a full cationic charge will be available for the oscillation in the x direction, since the quaternary ammonium group will not participate in the oscillating system. The triene (VI) absorbs at a much lower frequency than the linear triene (VII). In (VI) the opening of the central double bond forces a positive or negative charge into the rest of the molecule. The former possibility is illustrated in (VI A) and (VI B), and the increase in the charge, with the oscillation of which the color is associated, leads to the bathochromic effect.[9]

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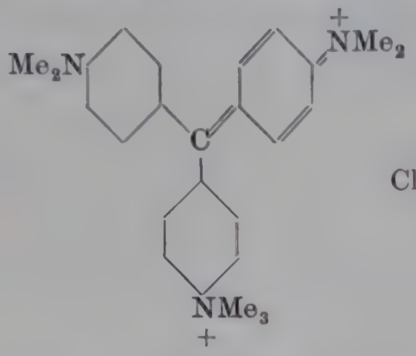
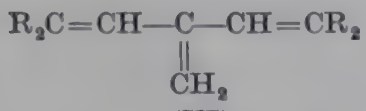
[70] See p. 363.

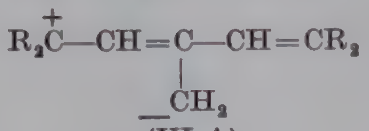


Cl_2^{--} (V)



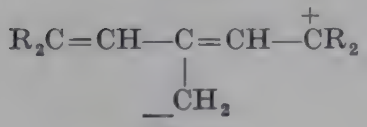
$R_2C{=}CH{-}\underset{\underset{CH_2}{\|}}{C}{-}CH{=}CR_2$

(VI)



$R_2\overset{+}{C}{-}CH{=}\underset{\underset{{}^{-}CH_2}{|}}{C}{-}CH{=}CR_2$

(VI A)



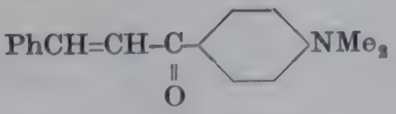
$R_2C{=}CH{-}\underset{\underset{{}^{-}CH_2}{|}}{C}{=}CH{-}\overset{+}{C}R_2$

(VI B)

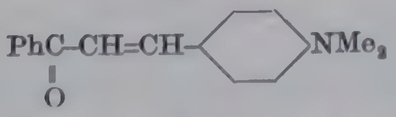
$R_2C{=}CH{-}CH{=}CH{-}CH{=}CR_2$

(VII)

Another example is provided by (VIII) and (IX); the x band has λmax 4,190A. for (IX) and λmax 3,870A. for (VIII); while the y band has λmax 2,640A. for (IX) and 3,030A. for (VIII), in accordance with the increase in the polarizability along the y axis of (VIII).[75]



(VIII)



(IX)

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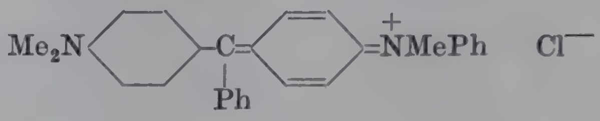
[9] See p. 326.

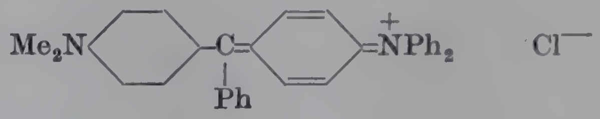
[75] Katzellenbogen and Branch, *ibid.* **69**, 1615 (1947).

Diaminotriphenylmethane dyes have a spectrum between 8,000 and 2,400A. consisting of three principal bands, *x*, *y*, and *x′* (second order) bands. When one or more methyl groups in Malachite Green are replaced by phenyl groups, there is a hypsochromic displacement as would be expected from a consideration of the relative basicities of dimethylamine and diphenylamine. However, the values of λmax for the *x* or *y* band of the unsymmetrically substituted analogs (X) and (XI) deviate very slightly from the calculated values.[76] In Fig. 16 curves 1 and 2 respectively represent the spectra of (X) and (XI), and the arrows show the mean of

(X)



(XI)



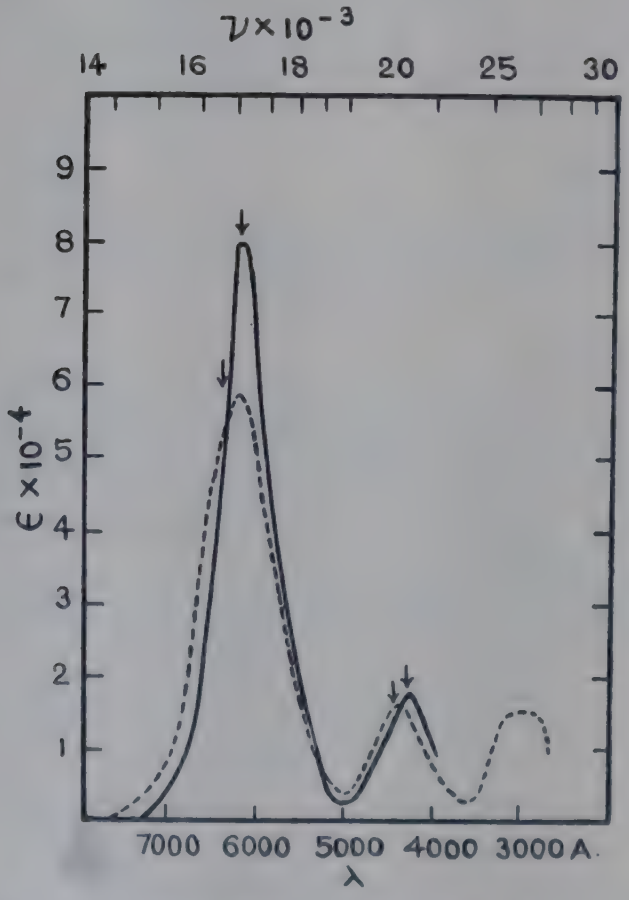


Fig. 16. The Brooker deviation, absorption spectra in methyl alcohol $[R{=}C_6H_4C(C_6H_5)C_6H_4]$ of: ———, $[(CH_3)_2NRNCH_3C_6H_5]^+$; - - - - -, $[(CH_3)_2NRN(C_6H_5)_2]^+$. Arrows indicate mean values of λmax for the parent symmetrical dyes.

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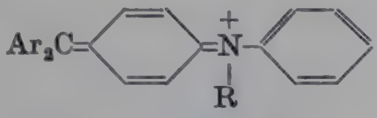
[76] The "Brooker deviation" is further explained later.

the wave lengths of the symmetrical dyes of which (X) and (XI) are the structural hybrids.[77] As Brooker has stated, the asymmetry of these dyes is definable in terms of the relative basicities of the auxochromic nitrogen atoms; this basicity in turn is defined more precisely in terms of resonance stabilization of the ring systems, of which the nitrogen atoms are a part or to which they are attached. In the quinonoid ion of a triphenylmethane dye, an *N*-phenyl group extends the conjugation as indicated in (XII), and this compensating factor results in the basicity of the nitrogen atom being reduced to a much smaller extent than it is by the *N*-phenylation of aniline.



(XII)

By examining under polarized light the absorption and fluorescence of crystals of polynuclear aromatic hydrocarbons (e.g., chrysene), Krishnan and Seshan[78] have shown that for such large planar molecules the absorption, as well as the fluorescence, is at a maximum when the electric vector of the light is parallel to the plane of the molecule, and at a minimum when the two are normal to each other. The crystals are suitable for studying the optical anisotropy of these molecules, since they retain their individuality in the crystal state and their orientations in the crystals are known from X-ray data. Raman has made the important generalization that "the types of molecular structure in carbon compounds which favor the development of color are those which exhibit an exceptionally high degree of optical anisotropy."[79] Groups and structures which give rise to strong absorption also enhance the electrical and magnetic anisotropy of the molecule.[80]

In the absorption spectrum of anthracene (Fig. 17) the short wave group of maxima (a, b) and the long wave series of maxima (c–g) are respectively associated with electronic activations (cf. structures XIII A, B and C) polarized in two directions perpendicular to each other in the plane of the molecule. Comparing the spectra of anthracene and 9-anthraldehyde (XIV), in which the 9-aldehydo group effects a marked bathochromic shift of the long wave band, together with loss of fine structure, Jones[81] has suggested that the long wave band is associated with an electrical moment oriented approximately in a vertical direction (*y* band). Structure

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[77] Tolbert, Branch, and Berlenbach, *JACS* **67,** 891 (1945); see also Branch, Tolbert, and Lewis, *ibid.* 1693; Katzellenbogen and Branch, *ibid.* **69,** 1978 (1947).

[78] *Current Sci.* (*India*) **3,** 26 (1934); *Proc. Indian Acad. Sci.* **8A,** 487 (1938).

[79] *Nature* **123,** 494 (1929).

[80] Raman and Bhagavantam, *Indian J. Phys.* **4,** 57 (1929).

[81] Jones, *JACS* **67,** 2127 (1945); *Chem. Revs.* **41,** 353 (1947).

(XIV A) in which the negative charge is on an oxygen atom should be of considerably lower energy and make a much larger contribution to the excited state of 9-anthraldehyde than the corresponding structure (XIII A)

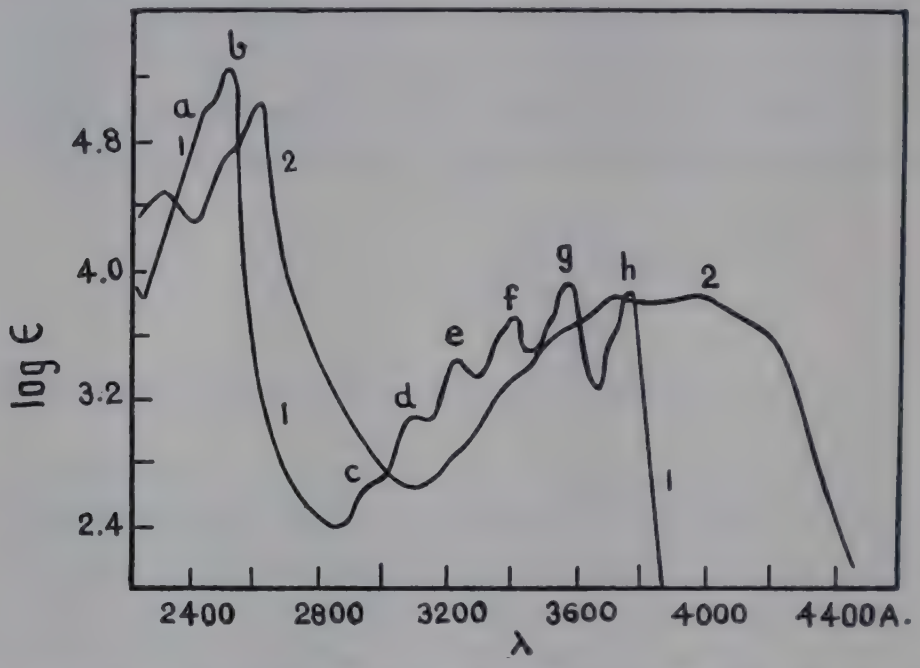
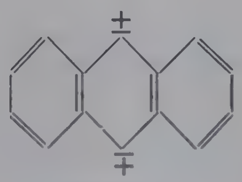
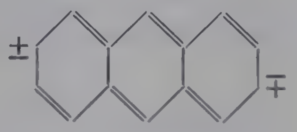


Fig. 17. Ultraviolet absorption spectra of (1) anthracene and (2) 9-anthraldehyde (solvent ethanol).

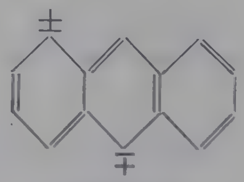
for anthracene; the result should be a larger displacement of an absorption band associated with an excitation along the y-axis than of a band associated with an electric moment oriented in the x or z direction. The difference



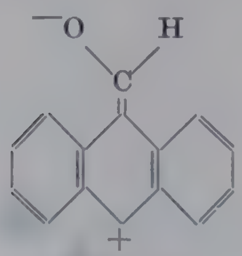
(XIII A)



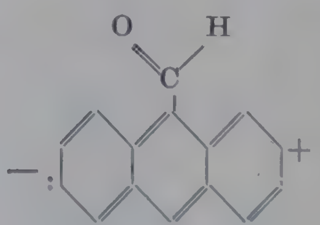
(XIII B)



(XIII C)



(XIV A)



(XIV B)

in energy between the structure (XIII B) for anthracene and (XIV B) for 9-anthraldehyde should be relatively small, and so is the shift in the short-wave band (x band). Another consideration that confirms this suggestion of Jones is a comparison of the dipole moments of structures (A) and (B) for anthracene (XIII), computed as 15.0 D and 34.5 D respectively. Intensities of absorption are directly related to dipole moments, and the larger dipole moment of (B) clearly indicates that x-polarization gives rise to the short-wave high-intensity band; and y-polarization, which has a smaller dipole moment, gives rise to the long-wave low-intensity band.[81a]

Applying the method of molecular orbitals to the ultraviolet absorption of the polyacene series (naphthalene to pentacene) Coulson[82] has shown that the longest wave length in an allowed excitation probably arises from a transition between mobile electron levels of symmetry $A_{1g} \longrightarrow B_{2u}$, and polarized across the width of the molecule. The second wave length is due to a transition $A_{1g} \longrightarrow B_{1u}$, polarized along the length of the molecule. The Lewis-Calvin theory, according to which the oscillation of least energy should be along the length of the molecule, is thus invalid for the polyacene type of molecule, although it holds good for the polyenes in which the red shift is associated with lengthwise oscillations. According to the valence-bond method,[83] in which the ground state and the lowest excited states are regarded as combinations of the Kekule structures, there can be no transition in the y direction; but if the ionic structures (such as A, B and C for anthracene) are included as contributing largely to the excited state,[84] the conclusions of the valence-bond and molecular orbital methods are comparable.[82, 85] Structures such as A will contribute to y-polarization; B mainly to x-polarization; and C to both. Since A contains two benzenoid rings, while C has only one and B none, A represents a structure of relatively low energy, so that the y-transition will give rise to the long wave absorption.

SECOND ORDER BANDS

In the quasi-classical theory of Lewis and Calvin, excitation by light produces an oscillation of the electron cloud in a definite direction along the x or the y axis. This may be regarded as a (quantized) alternating current along the axis. A higher excitation results in a second oscillation of greater amplitude. There are cases of " forbidden " excitations to states which are not in the same class as the ground state (e.g., having a different multiplicity), but Lewis has pointed out that such transitions are not found in the ordinary spectra of dyes. In the absorption curves of various carotenoids there is a band in the ultraviolet which Lewis and Calvin consider to be a second order band (x' band). A characteristic band of short wave length in the spectra of the diphenylpolyenes is likewise regarded as second order absorption.[86] Kumler[87] regards the second bands (λmax 2,040–2,750A.) in the spectra of a series of *p*-disubstituted benzene derivatives as *x*′ bands; the *x* bands have λmax 2620–4280A. The *x*′ bands which, like the first order bands, belong to the fundamental oscillation of the molecule as a whole, are ordinarily obscured by the bands of partial oscillation. However, in dyes for which the *x* bands are in the red region, definite evidence of *x*′ bands has been obtained. Lewis and Bigeleisen[88] have found that the eight dyes in Table III show unambiguous *x*′ bands. The *x*′ band in the curves for Fluorescein, Rhodamine B and Malachite Green (see Fig. 15, curve 3) was identified and differentiated from the neighboring *y* band by the method of fluorescent polarization. The dyes in Table III are a remarkable series in which ε'/ε is always large, and ν'/ν increases almost regularly with increasing wave length of the band. This is the trend predicted by Lewis and Calvin from their potential diagram for electronic displacements in dye molecules that have left and right symmetry.

[81a] Govinda Rau and Venkataraman, *Current Sci.* (*India*) **19**, 9 (1950).

[82] *Proc. Phys. Soc. London* **60**, 257 (1948). See also Klevens and Platt, *J. Chem. Phys.* **17**, 470 (1948).

[83] Förster, *Z. physik. Chem.* **B41**, 287 (1938).

[84] A. and B. Pullman, *Experientia* **2**, 364 (1946).

[85] Craig, *Compt. rend.* **227**, 126 (1948).

TABLE III

	Solvent	ν/cm.$^{-1}$	ν'/cm.$^{-1}$	ν'/ν	ε'/ε
1. Fluorescein	Dilute alkali	20400	35100	1.72	0.144
2. Rhodamine B	Dilute alkali	18000	32300	1.80	0.137
3. Crystal Violet (A)	Ethanol	16940	32900	1.94	0.258
4. Michler's hydrol	Glacial acetic acid	16670	33300	2.00	0.165
5. Malachite Green	Ethanol	16000	31700	1.98	0.197
6. Methylene Blue	Ethanol	15200	30700	2.02	0.109
7. Capri Blue	Ethanol	15100	32750	2.17	0.153
8. Methylene Blue (D^1H^{++})	$3M$ H_2SO_4	13500	29500	2.20	0.110

The relation between the geometry of molecules and their spectral characteristics has been extensively studied in the case of the carotenoid pigments.[89] A natural all-*trans* carotenoid pigment is partly converted by heat or treatment with iodine into a mixture of *cis-trans* isomers, and the isomerization results in a decrease in the intensities and wave lengths of the absorption maxima.[90] Among all the stereoisomers of a polyene, the all-*trans* form, possessing the extended planar structure, must have the greatest depth and intensity of color. However, in a part of the spectral region (3,600A.), a new absorption maximum (the "*cis*-peak") appears when isomerization to the *cis*-arrangement occurs at one or more of the ethylenic bonds, so that the shorter, folded molecule acquires a breadthwise extension. The *cis*-peak (Fig. 18) has maximum intensity in neolycopene A (Fig. 19). Zechmeister and Pauling have proposed a theoretical interpretation of the *cis*-peak phenomenon, in which the observed absorption spectra of the carotenoids are correlated with transitions from the normal electronic state to three excited electronic states (Fig. 20).[91] The transition 0——→1 corresponds to the fundamental absorption band (near 4,700A.

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[86] See also Heilbron, Jones, and Raphael, *JCS* 139 (**1944**).

[87] *JACS* **68,** 1184 (1946).

[88] *Ibid.* **65,** 2107 (1943).

[89] Zechmeister, *Chem. Revs.* **34,** 267 (1944); Pauling, *Helv. Chim. Acta* **32,** 2241 (1949).

[90] Pauling, *Fortschr. Chem. Organ. Naturstoffe*, **3,** 203 (1939); Mulliken, *J. Chem. Phys.* **7,** 364 (1939); *Revs. Modern Phys.* **14,** 265 (1942).

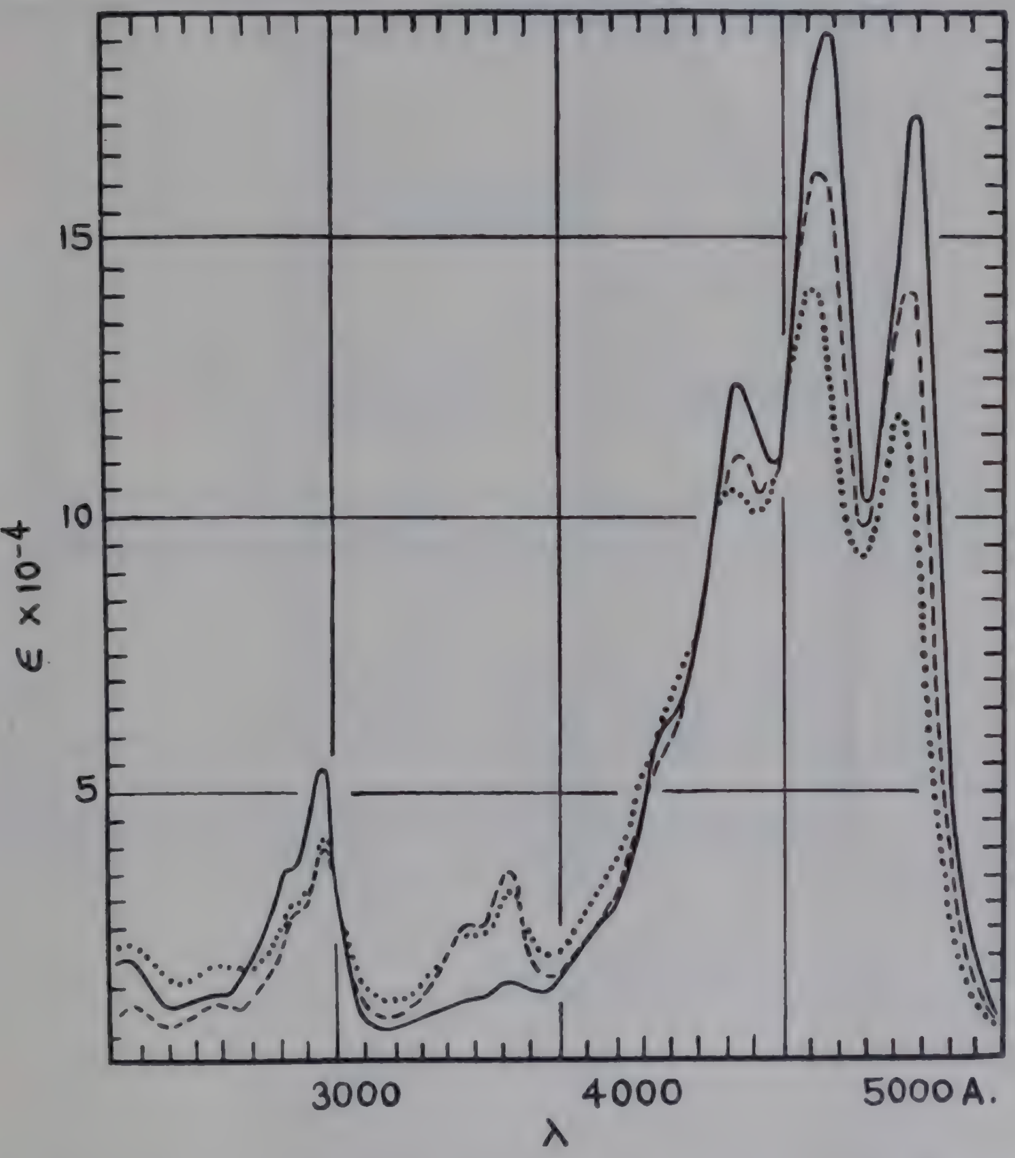

Fig. 18. Molecular extinction curves of lycopene in hexane: ———, all-*trans* form; – – – –, after refluxing in the dark for 45 minutes; . . . . . ., after iodine catalysis at room temperature.

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[91] Zechmeister *et al.*, *JACS* **65**, 1940 (1943).

in Fig. 18 for lycopene), 0—→2 to the *cis*-peak, and 0—→3 to the third band (near 2,900A.). The bands are broad, and show a pronounced fine structure. Quantum-mechanical calculations indicate that the three transitions correspond to oscillation of electric charge along the unsaturated chain in the ways shown in Fig. 21. The simple oscillation from end to

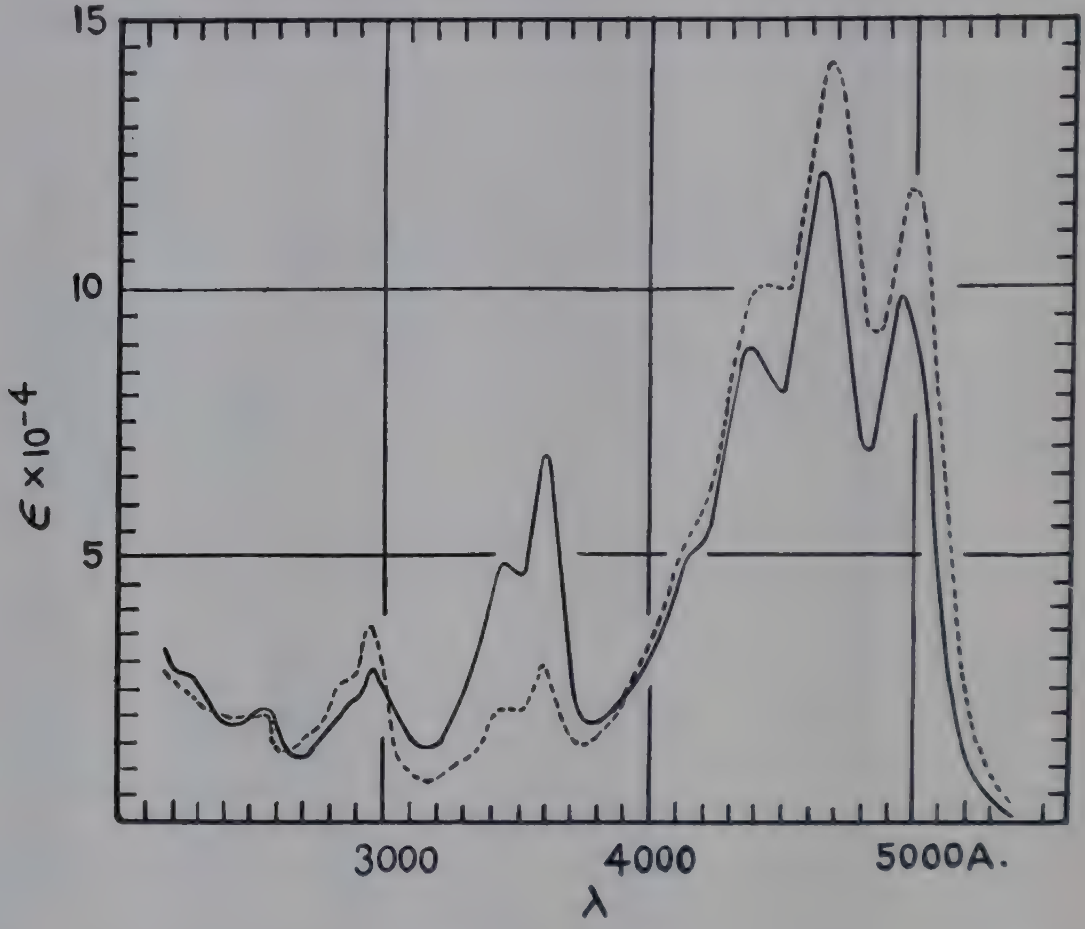


Fig. 19. Molecular extinction curves of neolycopene A: ———, without iodine; ————, on iodine catalysis.

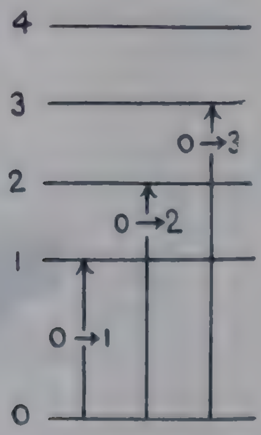


Fig. 20. Electronic energy levels for a carotenoid molecule, with the transitions indicated corresponding to the three main absorption regions (0——→1, fundamental absorption region; 0——→2, "*cis*-peak" region or first overtone; 0——→3, second overtone).

end of the chain corresponds to the transition 0⟶1. The next mode of oscillation of the electrons is from the two ends of the chain to the middle, and from the middle towards the two ends; the 0⟶2 oscillation therefore

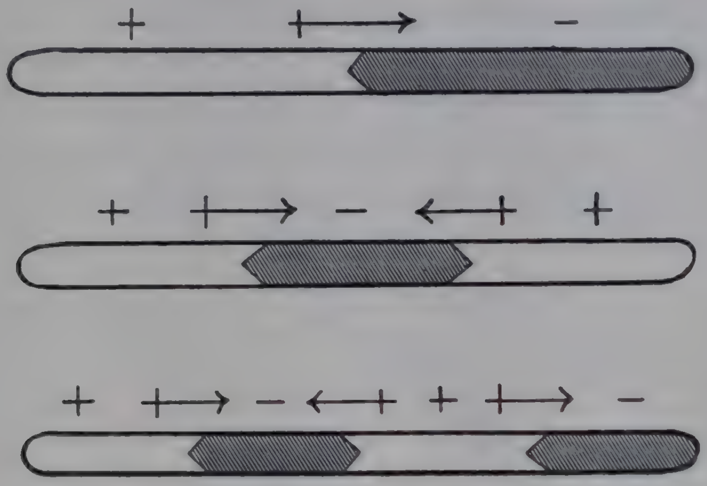


Fig. 21. Diagram indicating classical modes of vibration of mobile "unsaturation" electrons of the conjugated system along the chain. The three modes shown correspond to the three main regions of absorption of light by carotenoids.

gives rise to no dipole moment, and hence to no absorption band, for the all-*trans* molecule, or for any other molecule with a center of symmetry. The molecule which is *cis* at the central double bond, represented diagrammatically in Fig. 22, has a dipole moment for the transition 0⟶2 because of its shape, the moment being perpendicular to the line *AB*. This isomer

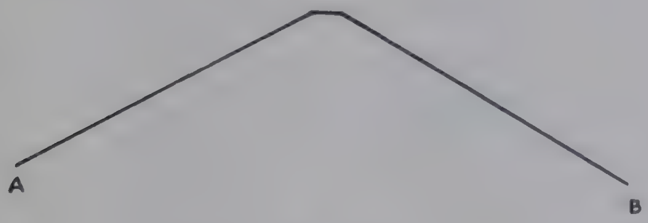
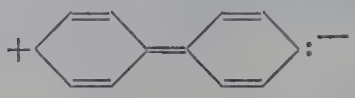


Fig. 22.

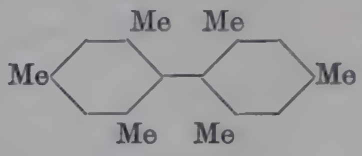
should show the strongest *cis*-peak among all the isomers, and is identified among the lycopenes with neolycopene A. The *cis*-peaks for other isomers will be of lower intensity, and as a rough approximation, the intensity can be taken to be proportional to the square of the distance between the center of the conjugated system and the midpoint of the straight line between the two ends.

STERIC FACTORS, RESONANCE AND COLOR

Since electronic oscillations through a molecule as a whole and consequent increase in light absorption depend on the extent of the conjugation, steric factors which diminish or inhibit the conjugation will have a corresponding effect on light absorption. This postulate regarding the relation between decrease in light absorption and the steric weakening or inhibition of resonance has been verified for many compounds. The absorption of diphenyl is concerned with the contribution made by structures such as (I) to the excited states of the molecule. A planar configuration is necessary for the resonance to be completely effective, and there is evidence that in the absence of steric hindrance the molecule tends to be planar. When the two benzene rings are forced into different planes as in dimesityl (II), the absorption corresponds to that of mesitylene and not diphenyl.[92] The alteration in the absorption spectrum is more pronounced when the blocking groups in the *o*-positions are larger.[93]



(I)



(II)

Anthracene, 9-phenylanthracene, and 9,10-diphenylanthracene have very similar absorption spectra, because the meso-phenyl groups are sterically prevented from becoming coplanar with the anthracene nucleus so that resonance as in diphenyl is not possible; but the absorption spectra of 1,4,9,10- and 1,4,5,8-tetraphenylanthracenes show that specific arrangements of the phenyl groups may cause such a distortion of the anthracene nucleus that the molecule can be monoplanar and permit, therefore, the occurrence of resonance phenomena.[94, 95] However, other evidence in support of such a possibility must be sought.

From the absorption curves of *trans*- and *cis*-stilbene (Fig. 23)[96] it will be observed that the *cis*-compound absorbs at higher frequency and lower intensity than the *trans*. The *trans*-stilbene molecule is planar, and the resonance effect is shown by the position and intensity of the fundamental band. Coplanarity is prevented in *cis*-stilbene by the interference of the *o*-hydrogen atoms and as a result of the weakening of the optically important resonance, the light absorption is diminished.[97]

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[92] Pickett, Walter, and France, *ibid.* **58,** 2296 (1936); see also Ferguson and Robinson, *ibid.* **71,** 742 (1949).

[93] Williamson and Rodebush, *ibid.* **63,** 3018 (1941).

[94] Jones, *ibid.*, **67,** 2127 (1946); Hirshberg, *Trans. Faraday Soc.* **44,** 285 (1948).

[95] For a study of steric hindrance effects in naphthalene derivatives, see Friedel, Orchin, and Reggel, *JACS* **70,** 199 (1948).

[96] Smakula and Wassermann, *Z. physik. Chem.* **A155,** 353 (1931).

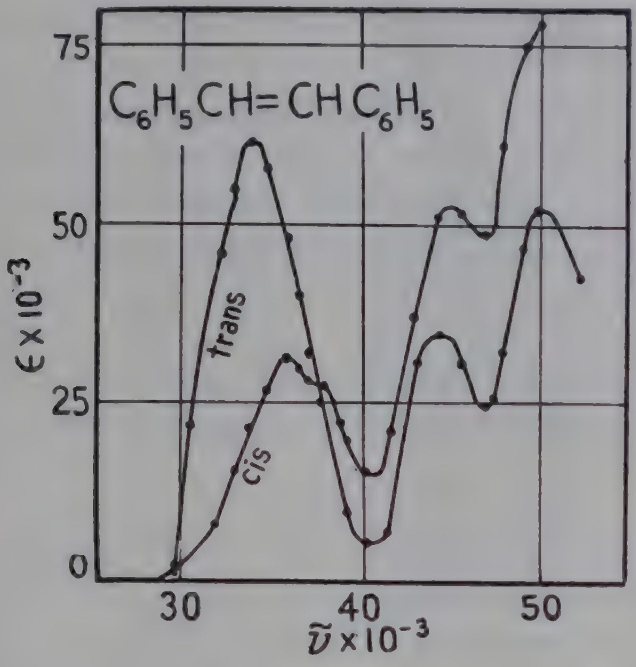
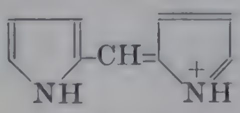


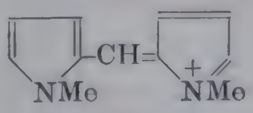
Fig. 23. Absorption curves of the *cis* and *trans* forms of stilbene (Smakula and Wassermann).

In the disazo dyes derived from benzidine, increased insulation at the 1,1′-(diphenyl) bond appears when noncoplanarity is induced by the substitution of methyl groups in the 2,2′-, and 2,2′,6,6′-positions.[98] The nonlinearity of the 2,2′-dihydroxybenzalazine molecule results in a splitting of the main absorption band of the 4,4′-isomer into two bands, one of shorter and the other of longer wave length.[99]

There are conditions under which steric hindrance to planarity in dye molecules (e.g., crowding the two nuclei of a cyanine out of a common plane)[100] results in the shifting of the absorption maximum to longer wave length. The ion (III) has λmax 4,700A., while (IV) has λmax 5,100A.;



(III)



(IV)

(III) can be coplanar with a slight bending of the N–H bonds, but the methyl groups in (IV) preclude coplanarity of the two pyrrole rings. The departure from planarity raises the potential energy of (IV) in the ground state, so that the difference in the energies of the ground and excited states becomes smaller and absorption occurs at longer wave length.[101]

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[97] See also Wiegand and Merkel, *Ann.* **557**, 242 (1947).

[98] Brode and Morris, *JACS* **70**, 2485 (1948); *J. Org. Chem.* **13**, 207 (1948).

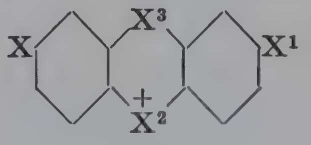
[99] Blout and Gofstein, *JACS* **67**, 15 (1945).

[100] Brooker *et al.*, *Chem. Revs.* **41**, 325 (1947).

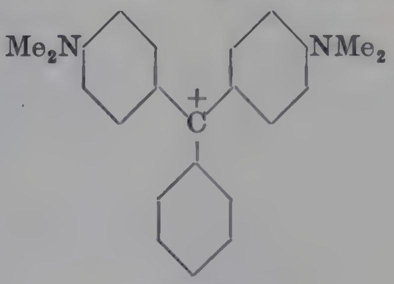
These interrelated factors of resonance, coplanarity, and color are also concerned in the absorption of dyes by cellulose (see Chapter XLI).

USE OF QUASI-CLASSICAL METHODS FOR CALCULATING ABSORPTION SPECTRA

The functional nature of the curves obtained by plotting the wave length of maximum absorption against the number of double bonds in certain polyenic compounds and symmetrical cyanines has been discussed earlier in terms of the Lewis-Calvin quasi-classical theory. The theory has also offered a qualitative solution of many problems concerning the color of dyes, and in a recent extension of his ideas to a large family of dyes represented by the skeleton formula (I) Lewis[102] has succeeded in calculating the wave length of the main absorption band by two rules. For more than seventy dyes the difference between the calculated and observed values was less then 30A. Where the discrepancies were larger, they were explicable by the amplifications which had to be adopted in obtaining the constants required for the determination.



(I)



(II)

The rules are that (1) the wave length is always greater, the greater the fraction of the characteristic positive charge on the auxochromes (this rule would appear to be the same as "the steeper the energy gradient between extreme and intermediate resonance structures the deeper the color" rule in Fig. 25); and (2) the effect of various groups on wave length is additive. The second rule is empirical, and both the rules are obviously inapplicable to such large and important groups of dyes as the azo, indigoid, and anthraquinone dyes.

According to the Lewis theory, an excited state produced by the absorption of light is characterized by an oscillation of the electronic cloud along some axis of the molecule, and in Malachite Green (II) the first absorption band corresponds to a horizontal oscillation, and is the *x* band as defined earlier. The characteristic positive charge formally assigned to the central carbon atom in (II) is distributed by resonance to various parts of the molecule, chiefly to the two NR_2 auxochromes. Since all the molecules in this family have about the same horizontal dimension, it is postulated that the wave length of the x band depends solely on the fraction of the characteristic charge on the two auxochromes. Any influence which increases this charge increases the wave length, and any influence which decreases the charge decreases the wave length. It can be readily seen that the rule agrees qualitatively with available data. Thus when X^3 is O, S, or NR in (I), there is a shift towards lower values of wave length, owing to the basic character of these groups; they acquire part of the characteristic charge and leave less available for the auxochromes. A strong positive effect is noticed when at X^2 we replace CR by N. In the former type (II) represents one of the important resonance structures of the molecule; but in Methylene Blue (III) will only make a very minor contribution to the resonance since nitrogen has much less tendency than carbon to act as an acid, and for Methylene Blue $\lambda = 6{,}650$A. When a proton is added to the central nitrogen in Methylene Blue, any characteristic charge remaining on the nitrogen is driven into the rest of the molecule, so that for Methylene Blue in strong acid $\lambda = 7{,}420$A.

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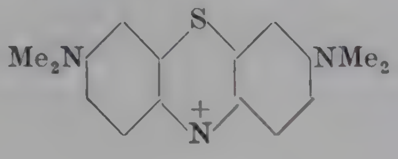
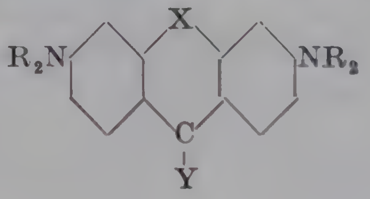
[101] Brunings and Corwin, *JACS* **64**, 593 (1942).
[102] *Ibid.* **67**, 770 (1945).



(III)

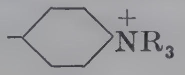
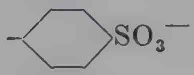
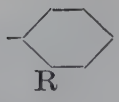


(IV)

The observation that any change in X and X^1, or in X^2 or X^3, produces the same change in wave length, regardless of the character of the rest of the molecule (I), has enabled Lewis to obtain additive constants by means of which known absorption maxima could be correlated and new ones calculated. Taking NR_2 as the standard auxochrome, ignoring the minor changes in wave length due to various alkyl and aralkyl groups, and taking as the standard dye a dye of the Malachite Green type (IV; in which X is absent), the following constants have been computed for various structural changes introduced in a dye of the general form (IV).

Although according to chemical evidence O^- is more basic than NH_2, the two exhibit about the same auxochromic effect in this series of dyes. When the p-position in the unsubstituted phenyl group of Malachite Green (II) is occupied by $\overset{+}{N}H_3$ or $\overset{+}{N}R_3$, the coulombic effect drives a part of the characteristic charge towards the NR_2 groups, and there is an increase in wave length. When the p-position is occupied by SO_3^-, the coulombic effect is in the opposite direction, but it is more than offset by the conjugation of the acid group, which tends to drive part of the characteristic charge towards the NR_2 groups. This effect, however, is less than that of the NO_2 group. An *o*-substituent in the unsubstituted phenyl group of Malachite Green has an interesting steric effect; it forces the phenyl group away from the nearly coplanar configuration and diminishes its contribution to the general resonance, so that the positive charge on the NR_2 groups is increased with a consequent increase in wave length.

TABLE IV

Structural change in (IV)	*Shift in* λ *in A.*
Replacement of R by H	−130
Replacement of both NR_2 by O^-	−690
X=O or S	−720
X=NR	−1570
Replacement of CY by N	+1080
Y= 	+140
Y= 	+60
Y=  (R=Me, Cl, etc.)	+110

The only class of dyes in which Lewis found a marked discrepancy between the observed and calculated value of wave length was the acridine type (IV; X=N; Y=H). This is also the only class in the whole family of dyes of the general formula (I) in which there is a large part of the characteristic positive charge on both X^2 and X^3. It is therefore likely that in the acridine dyes the electronic oscillation of lowest energy, corresponding to the first band, is not the horizontal but the vertical one. The calculated values would then be not for the first or long wave band, which here (as in anthracene discussed earlier) is the *y* band, but for the second or medium wave band, which is the *x* band. In fact, for Acridine Yellow (3,6-diamino-2,7-dimethylacridine hydrochloride), Formanek found a second band at 4,170A. in close agreement with the value of 4,110A. calculated by Lewis.

DEGENERACY OF LIMITING STRUCTURES IN RELATION TO ABSORPTION

If a system can be described by more than one state of the same energy (e.g., the two states of the hydrogen molecule), it is said to be "degenerate." The greatest resonance interaction occurs between totally degenerate states, and the degree of degeneracy depends on the number of identical energy states and the energies of the other states which contribute to the resonance.

Other factors being equal, deep colors are associated with dyes to which structures having a high degree of degeneracy may be assigned. Conversely, if the degeneracy of the important resonance structures which can be formulated for a dye is diminished by decreasing the symmetry of the molecule, the result is absorption at shorter wave lengths. In symmetrically constituted dyes such as Malachite Green, the extreme low-energy structures are identical, and the quantum-mechanical degeneracy of the structures is complete. Brooker has studied a series of cyanine dyes for which it is not possible to devise two identical limiting structures, and he has shown that nonidentity of the extreme resonance structures may have a very profound influence on the absorption of a dye.[36, 103]

Vinylene shift. Like the diphenylpolyenes, there are other types of compounds containing conjugate chains, in which it is possible to increase the length of the chain by adding further vinylene (–CH=CH–) groups. The dyes therefore possess the general form A(–CH=CH)$_n$–B, and as explained in discussing the diphenylpolyenes, a bathochromic shift takes place as n is increased. This *vinylene* shift, however, varies in amount

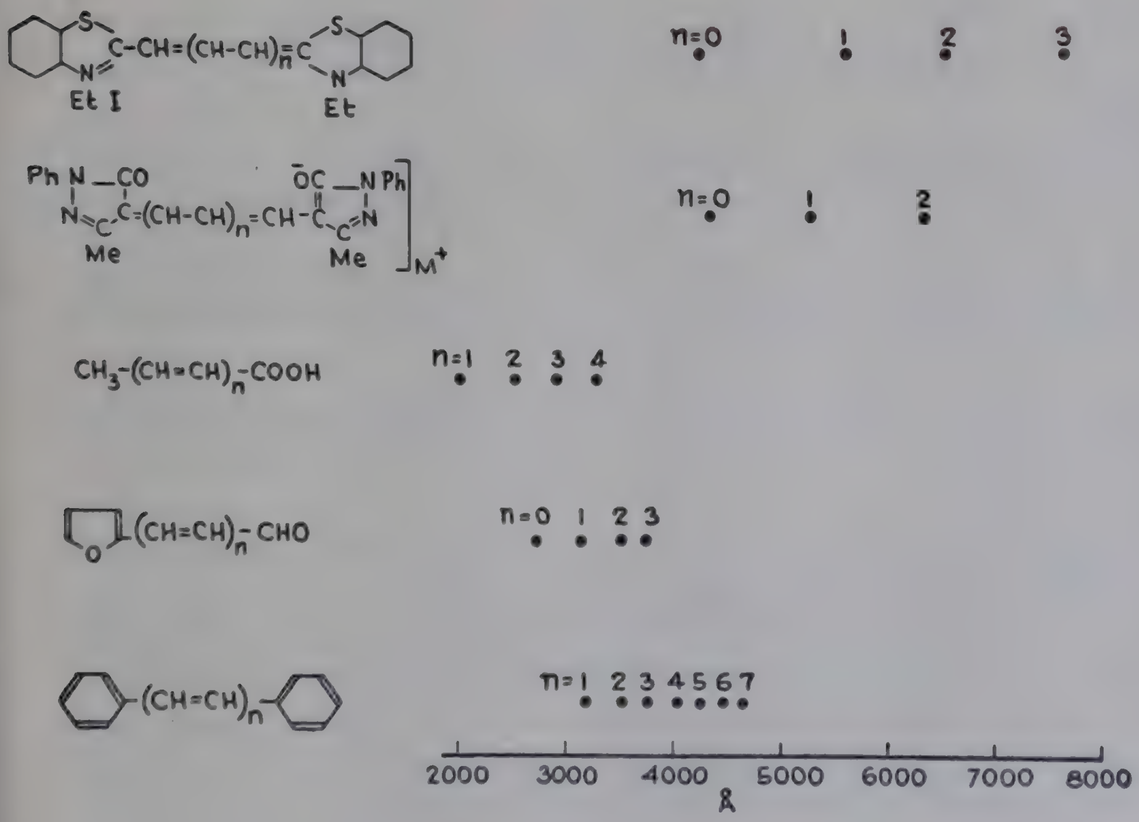


Fig. 24. Absorption maxima in A. (λmax) of five vinylene homologous series: (I) and (II) in methanol; (III) and (IV) in ethanol; (V) in benzene solution.

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[36] See p. 343.

[103] *Revs. Modern Phys.* **14,** 275 (1942).

from series to series in which A and B are differently constituted. The absorption maxima of five such series[103] are shown in Fig. 24. The first two series (I and II) represent symmetrical polymethine dyes, in which the successive shifts are large, and the shift per vinylene unit is approximately constant. These two series are nonconvergent. In the last three series (III, IV, and V), which are described as convergent, the bathochromic shift per vinylene unit is much smaller than in the nonconvergent series, and the successive shifts tend to diminish as *n* increases. In vinylene series for which the extreme low-energy structures are nondegenerate the maxima are therefore convergent.

Quantum-mechanical considerations applied to a system of the type of (VI) have shown that, as the chain is lengthened, the resonance splitting of the identical energy levels of the limiting structures decreases, as represented diagrammatically in Fig. 25. The resonance stabilization therefore diminishes as the series is ascended; and this is an important example of increasing depth of color in a series with decreasing resonance energy. In the polyenes (e.g., V) the resonance energy increases with *n*, as also the depth of color.

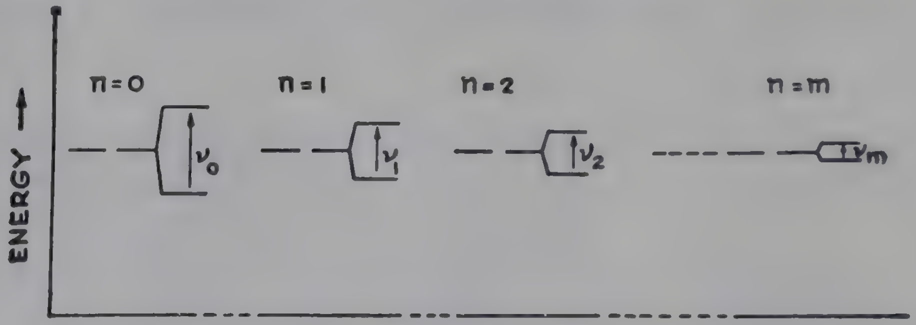

Fig. 25. Roughly qualitative representation of the resonance splitting of the energy levels of a vinylene-homologous series of symmetrical cyanine dyes such as VI (Brooker).

For many unsymmetrical cyanines such as (VII), λmax lies very close to the arithmetic mean of the values of λmax for the two symmetrical dyes (VI) and (VIII), of which (VII) can be regarded as a structural hybrid. If, however, a nitro group is introduced in the 6-position of the benzothiazole ring in (VII), the absorption maxima of the new dyes (IX) no longer agree with the calculated mean of the maxima for (VIII) and (X) of which (IX) is a structural hybrid. There is a considerable deviation in λmax between the observed and calculated values. The observed absorption is at shorter wave length, and the deviation increases with *n*. When $n=2$, the deviation is so great (675A.) that the unsymmetrical dye absorbs at shorter wave length than either of the parent symmetrical dyes. Brooker has shown that the deviation is due to the imbalance of the basicity of the heterocyclic nuclei in (IX), as a result of the lowering of the basicity of the benzothiazole system by the introduction of the nitro group. The more strongly basic quinoline ring exercises a more powerful attraction on the positive charge, so that structure A for (IX) becomes the dominant structure and produces a convergent series.

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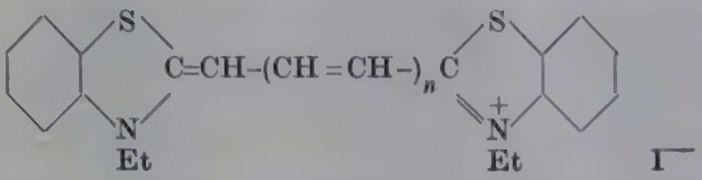
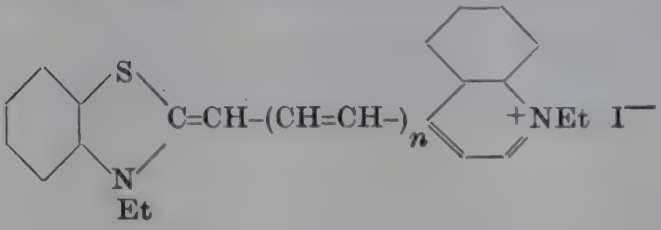
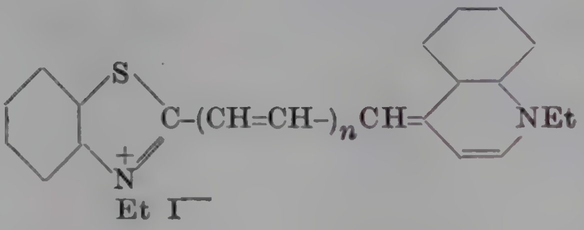
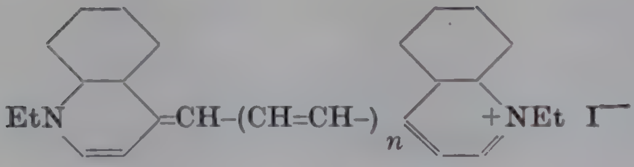
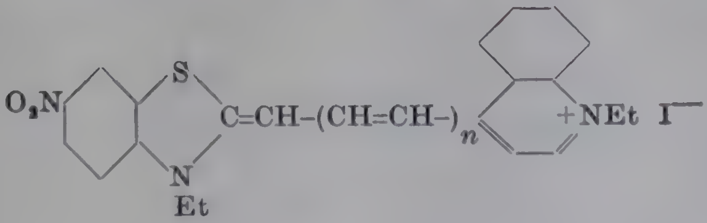
[103] See also p. 381.

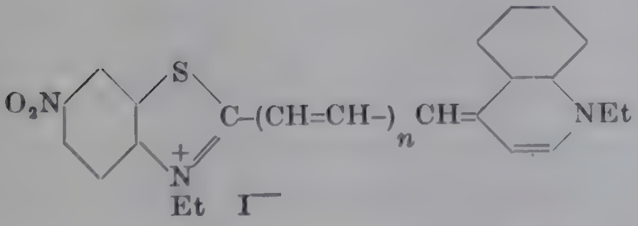

(VI)

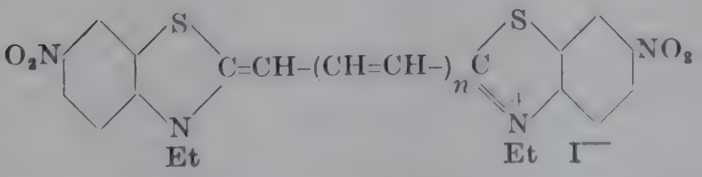

(VII A)


(VII B)

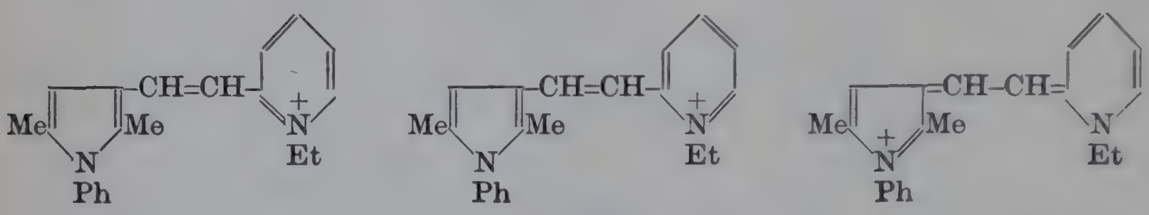

(VIII)


(IX A)


(IX B)


(X)

Additional-double-bond stabilization of rings. The greater attraction of one of the heterocyclic rings for the positive charge in an unsymmetrical cyanine, which determines the "Brooker deviation," is not to be identified with basicity in the usual sense of proton affinity, although they are related. By considering the principal resonance structures of the ion of a highly unsymmetrical dye, e.g., (XI A, B and C), it is seen that (A) and (B) comprise a closely related set of structures which together contribute to the pyridinium formulation and render it of lower energy than the pyrrolinium structure. The system thus becomes nondegenerate, and absorption occurs at markedly shorter wave length than that calculated.

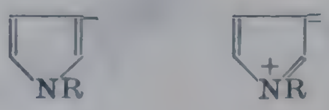


(A) (B) (C)

(XI)

The extra stabilization of the structures (A) and (B) is essentially due to the benzenoid stabilization of the pyridine ring; in (C) the uncharged pyridine ring has a low resonance stabilization like dihydrobenzene. Brooker refers to the extra stabilization resulting from the entry of an additional double bond into the ring as *adbs* (additional-double-bond stabilization). In a symmetrical cyanine the *adbs* of each ring is obviously the same; and unsymmetrical cyanines such as (VII) which show no deviation are those in which the two rings have the same or nearly the same *adbs*. Increasing divergence in the values of *adbs* for the ring systems should give increasing deviation. Examining a large number of unsymmetrical cyanines in which one heterocyclic ring was unvaried and the other was one of fifteen different heterocyclic systems, Brooker found that the deviations, which varied from 45 to 855A., were in the order of increasing *adbs*, as predicted from a study of the resonance characteristics of the nuclei.

The *adbs* concept is not altogether satisfactory, since for instance in passing from (XII A) to (XII B) there is no increase in the number of double bonds within the ring.[104] Brooker has more recently[105] suggested the use of



(A) (B)

(XII)

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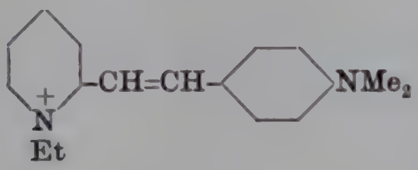
[104] Brooker, Private communication.

[105] *JACS* **67**, 1881 (1945).

the expression "N^{IV} minus N^{III} stabilization" for the difference in resonance stabilization between the rings with 4-covalent and 3-covalent nitrogen.

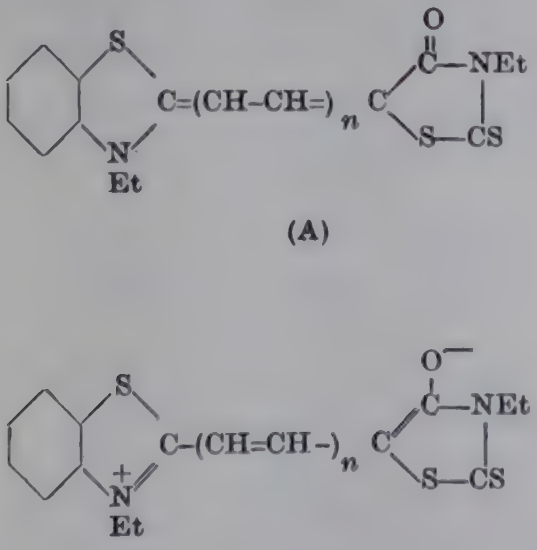
The effect of replacing one heterocyclic nucleus by another in the cyanines is governed by another generalization, the sensitivity rule: where a change of structure produces a small effect on the deviation of a symmetrical dye, the same change in structure produces a much greater effect on the deviation of a highly unsymmetrical dye. In other words, the effect on the deviation is greater the less the degeneracy of the extreme structures and the greater the deviation of the compound undergoing the change.

Brooker has shown that the conclusions reached in his study of the unsymmetrical cyanines are applicable to other convergent series, such as



(XIII)

the styryl dyes (XIII). The merocyanines (e.g., XIV) comprise by definition a nitrogen heterocycle linked to a moiety which contains a carbonyl group and which may or may not be cyclic. The absorption is accounted for by the resonance (A)$\longleftrightarrow$(B). The structure (B) is a dipole which should



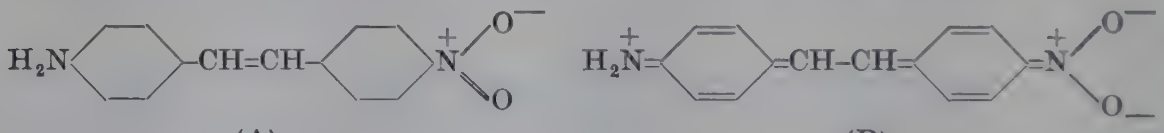
(A)

(XIV)

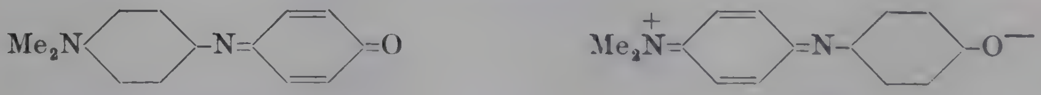
(B)

normally have considerably higher energy than (A); but both the heterocyclic rings have an additional double bond in the zwitterion structure, and this *adbs* in the two rings offsets the effect of the dipole to a greater or less extent. It is also interesting to note that, while high *adbs* of the nitrogen heterocycle corresponds roughly to high basicity, high *adbs* of the ring containing the C=O group corresponds to high acidity.

The *adbs* of rings is a useful consideration for assessing the relative stability of resonance structures, and this treatment of the merocyanines is applicable to other types of dyes involving resonance between uncharged and dipolar structures. Thus in 4-nitro-4′-aminostilbene (XV) both the benzene rings have higher resonance stabilization in the uncharged structure (A), and the absorption is at relatively short wave length.[106, 107] In Phenol Blue one of several factors involved in the depth of the color of this comparatively simple molecule is that the resonance stabilization of the two benzene rings taken together is the same in both the uncharged structure (A) and the polar structure (B).[15]

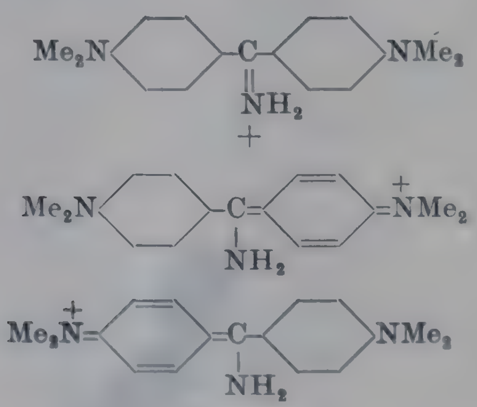

(A) (B)

(XV)


(A) (B)

Phenol Blue

The relatively weak color of Auramine is a related problem.[107] The ionic charge may be shared between the 3 nitrogen atoms (cf. A, B, and C), and apart from other considerations,[9] it is clear that the structure (A) will be strongly favored because both the benzene rings are in the benzenoid


(A)

(B)

(C)

Auramine

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[106] Calvin and Buckles, *JACS*. **62,** 3324 (1940).

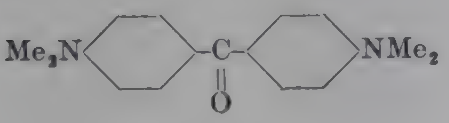
[107] Brooker and Sprague, *ibid*. **63,** 3203 (1941).

See p. 330.

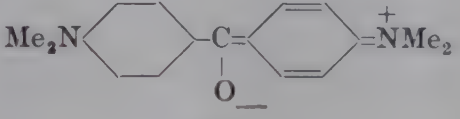
See p. 326.

state, and Auramine therefore absorbs at relatively high frequency. When the amino group is acylated,[108] the characteristic positive charge is transferred almost entirely to a dimethylamino group, so that structures (B) and (C) are stabilized, and the dyes are blue.[109]

The reactivity of groups and the color of many organic compounds often become explicable when the relative contributions of the benzenoid and quinonoid structures to the resonance of the molecule are considered. One example is the colorless character of Michler's ketone (XVI). In the resonance (A, B, C) which would determine the absorption characteristics

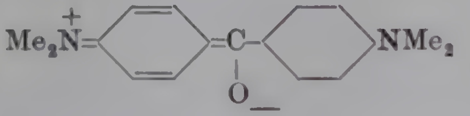


(A)



(B)

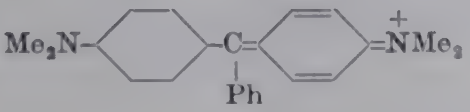
(XVI)



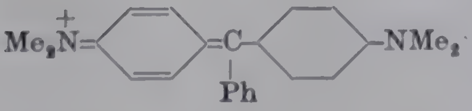
(C)

of the substance, the dominant structure will be A, in which both the rings are benzenoid; further, the energy of charge separation in structures B and C will be another factor diminishing their resonance contribution.[107]

Depth of color in relation to the energy difference between extreme and intermediate structures. As Adams and Rosenstein[11] and Bury[12] surmised, the intense color of a dye such as Malachite Green is associated with the resonance structures (A) and (B). The dye ion therefore has two identical low energy structures like benzene, with the difference



(A)



(B)

that in the dye the two extreme structures are derived by the movement of a charge from one end of the molecule to the other. Pauling,[110] however, has referred to the remote possibility of such a movement of an electron from end to end of a long conjugated chain, and he has suggested a series of

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[108] Semper, *Ann.* **381**, 234 (1911).

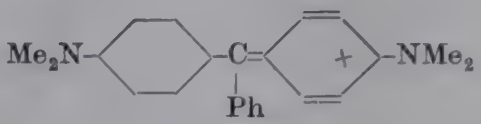
[109] Cf. Taylor and Baker, Sidgwick's Organic Chemistry of Nitrogen, Clarendon Press, Oxford, 1937, p. 96.

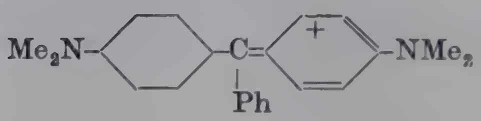
[107] See p. 386.

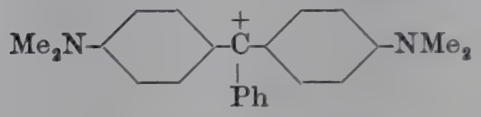
[11] See p. 327.

[12] See p. 327.

[110] *Proc. Natl. Acad. Sci. U.S.* **25**, 577 (1939).


(C)


(D)


(E)

Malachite Green

intermediate steps, such as (C, D and E), involving carbonium ions. These are much less stable than the ammonium ion structures; but by resonance interaction among these various structures, the difference in the energy levels of the ground state and the first excited state is small. The result

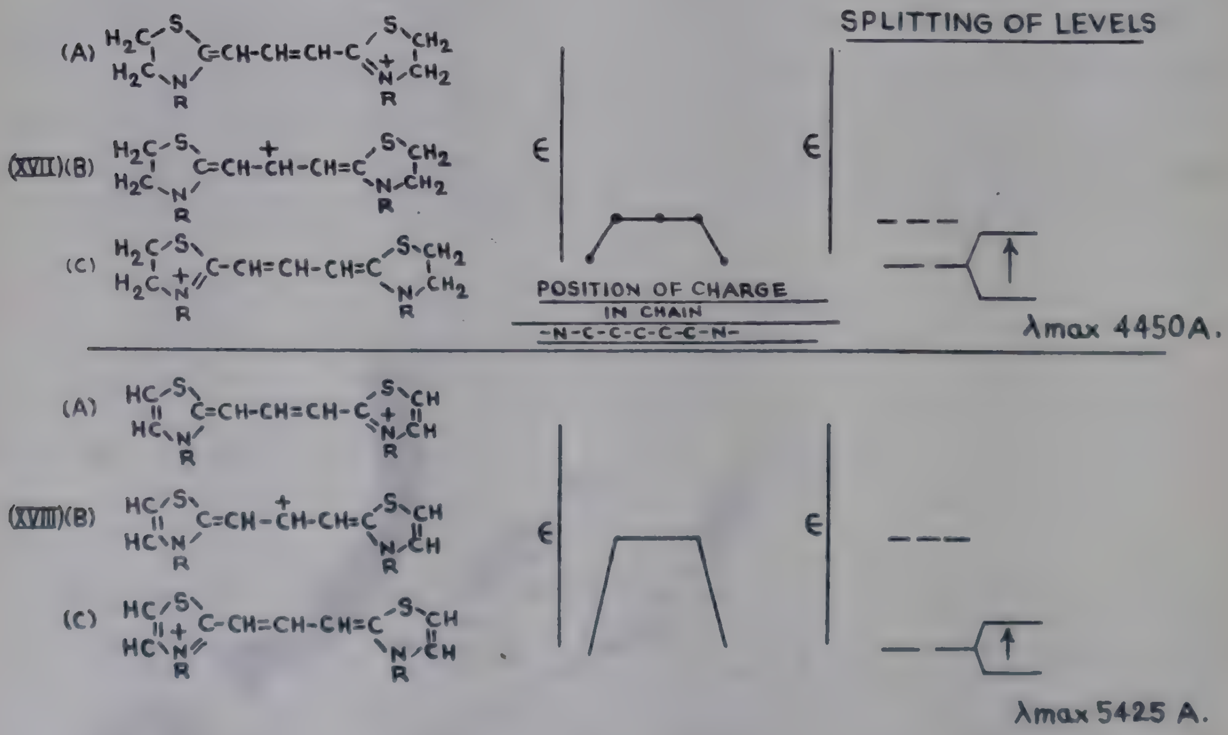

(A)
(XVII)(B)
(C)
ε
POSITION OF CHARGE IN CHAIN
-N-C-C-C-C-C-N-
ε
SPLITTING OF LEVELS
λmax 4450A.
(A)
(XVIII)(B)
(C)
ε
ε
λmax 5425 A.

Fig. 26. Comparison of two dyes of closely related structures. Rule: The steeper the energy gradient, the deeper the color (Brooker).

is the long wave absorption indicated by the green color; and with the high probability of the transition due to the large moment associated with it the intensity is also high.

When the absorption characteristics of a molecule are studied by taking intermediate structures into account in addition to the extreme resonance structures, as suggested by Pauling, one reason for the difference in absorption between closely related dyes becomes apparent.[36, 103] Two symmetrical cyanine dyes (XVII) and (XVIII) of the same chain length are compared in Fig. 26. The dye (XVII) of the upper formulas contains two thiazoline nuclei, and the other (XVIII) two thiazole nuclei. In each case, the two limiting structures are formulated, together with one of a number of intermediate structures. In (XVII) the carbonium structure (B) is not much higher in energy than the ammonium structures (A) and (C); the reduction in the resonance stabilization of the ring when the positive charge is transferred from N to C is not very great. Resonance splitting of the energy levels therefore will be relatively large, corresponding to the absorption of light of shorter wave length; the observed λmax is 4,450A. In (XVIII) on the other hand, passage from structure (A) to the carbonium structure (B) involves a considerable reduction in the resonance stabilization of the ring from which the positive charge is removed. The energy of (B) is therefore higher, relative to that of the extreme structures (A) and (C), than in the thiazoline dye (XVII). Consequently, the resonance splitting of the energy levels is smaller in (XVIII) and the absorption is at a longer wave length (5,425A.).

As a rule, among symmetrical dyes of closely related structure, the deeper will be the color, the steeper the gradient between the energy of the extreme resonance structures and the energy of the intermediate structures.

QUANTUM-MECHANICAL TREATMENTS

While the resonance concept has enabled us to understand certain broad relationships between the structure of molecules and their absorption spectra, a more quantitative approach has also been attempted in the case of a limited series of compounds.

Absorption spectra of benzene and polynuclear aromatic compounds. A study of the spectra of aromatic hydrocarbons and their

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[36] See p. 343.

[103] See p. 381.

derivatives is of obvious importance in dyestuff chemistry, since most dyes are derived from aromatic hydrocarbons.

The absorption spectra of numerous hydrocarbons have been measured[111, 81, 94] and, being characteristic of the particular system of fused aromatic rings, have been utilized for the identification of the hydrocarbons, for example, in connection with their carcinogenic properties.[84, 112] It is clear from Table V that the wave length of the absorption increases as the number of benzene rings is increased. This observation provides a simple device for increasing the depth of color in dye molecules; among the azo dyes for instance it is well known that naphthalene derivatives are deeper colored than the corresponding benzene analogs. The bathochromic displacement is greater in the linear hydrocarbons than in the angular isomers.

Clar[113] has found that for a series of linear benzenoid hydrocarbons the position of the absorption maximum of the lowest frequency (νp) is stated by equation (1), in which Rp is a numerical constant and n is the number of benzene rings. The reactivity (e.g., towards oxygen in the presence

$$\sqrt{\frac{Rp}{\nu p}} = n \qquad \dots\dots\dots \quad (1)$$

of light, maleic anhydride, etc.) of the linear condensed ring system also increases as the number of the rings increases.

The absorption spectra of some aromatic hydrocarbons have been calculated from quantum-mechanical principles. Both the molecular orbital (MO or LCAO) and the atomic orbital (AO; valence bond, VB) methods have been used in the treatment of the benzene molecule. In the first method, the orbitals of the π-electrons (the electrons of the "aromatic sextet") are considered and calculations made of the energies of a few of the lowest orbitals constructed by linear combinations of six equal atomic p orbitals with nodes coplanar with the ring. The second method utilizes the concept of resonance between valence-bond structures, the energy level being calculated[114, 115] in terms of a parameter α derived

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[111] Cf. Jones, *Chem. Revs.* **32,** 1 (1943).

[81] See p. 369.

[94] See p. 376.

[84] See p. 371.

[112] For a suggested correlation of electronic structure and carcinogenic activity of polynuclear hydrocarbons, see Pullman, *Bull. assoc. franc. étude cancer,* **34,** 245 (1947).

[113] *Ber.* **73,** 81, 104, 596 (1940); **76,** 257, 458 (1943).

[114] Sklar, *J. Chem. Phys.* **5,** 670 (1937); **7,** 984 (1939); **10,** 135, 521 (1942); *Revs. Modern Phys.* **14,** 232 (1942).

[115] See also Förster, *Z. Elektrochem.* **45,** 548 (1939).

by comparing the heats of hydrogenation of benzene and of cyclohexadiene (dihydrobenzene). The energy of a structure is lowered by $-\alpha$ (α being negative) when two electrons on neighboring atoms form a covalent bond, and it is raised by $-\alpha/2$ if they are not paired. The energy of a single Kekulé structure is therefore lowered by -1.5α (i.e., the energy is changed from 0 to $+1.5\alpha$) compared with a structure containing only single bonds. By resonance the identical energy levels of the two degenerate Kekulé structures split into a lower energy level (the ground state) and a higher energy level (the first excited state) which are calculated by a complicated mathematical process, and the difference of which is 2.4α.[116] The frequency of the first absorption maximum of benzene should then be $2.4\alpha/h$; taking α as 49 kcal. per mole, the wave length of the band would be 2,450A., in good agreement with the observed value of 2,550A. Similar quantum-mechanical calculations have been made for several polynuclear aromatic hydrocarbons by a consideration of the number and relative contributions

TABLE V

WAVE LENGTHS OF THE FIRST ABSORPTION BANDS OF HYDROCARBONS CALCULATED BY THE VB METHOD

Hydrocarbon	*λmax A.*		*Obs.*
	Calc. (Sklar)	*Calc. (Förster)*	
Butadiene	1900	—	2100
Hexatriene[117]	2570	—	2600
Octatetraene[117]	3120	—	3020
Fulvene	3650	—	3650
Benzene	2470	2450	2600
*cyclo*Octatetraene[118]	3320	3860	4000
Styrene	2570	—	2850
Azulene	6910	7800	6990
Naphthalene	2680	2950	2750
Diphenyl	2570	—	2515
Anthracene	—	3650	3700
Phenanthrene	—	3000	3400
Naphthacene	—	4500	4600
Pyrene	—	3450	3300
Pentacene	—	5450	5800

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[116] The difference between this figure and value of -1.5α for the lowering of energy in a single Kekulé structure is -0.9α, and this is the "resonance energy." When the three Dewar structures, which make a small contribution to the resonance of benzene, are taken into account, the resonance energy is slightly larger.

[117] M. Kovner, *Acta Physicochim. U.R.S.S.* **19,** 385 (1944); cf. *Compt. rend. acad. sci. U.R.S.S.* **35,** 54 (1942).

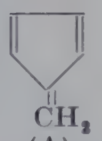
[118] Maccoll, *Nature* **157,** 695 (1946).

of the various canonical structures to the resonance states of the molecule. The calculated and observed wave lengths of the first absorption maxima for some hydrocarbons are stated in Table V.[28]

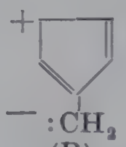
While there is a general agreement between the observed and the calculated values in spite of the approximations that have to be used in the mathematical process, it must be noted that the treatment is based largely on covalent structures and underestimates ionic structures. The significance of this limitation when applied to dye molecules will be apparent from the earlier discussion. The absorption bands associated with the excited states involving ionic structures are not calculable by this treatment, and the calculations therefore do not necessarily apply to the first absorption maxima. They may be assumed, however, to indicate that absorption will commence at a wave length at least as great as the calculated value. Daudel, Pullman and others have modified the valence-bond treatment to a " molecular diagram " method in which excited structures are included in the calculations.[84, 85, 119]

Fulvene and octatetraene (in comparison with benzene) and azulene (in comparison with its isomer naphthalene) provide examples of the dependence of light absorption on the relative resonance stabilization of the ground and excited states, and not on " resonance energy " as defined earlier. If resonance stabilizes the excited state more than the ground state, the absorption is shifted to longer wave length. The Kekulé structures mainly account for the resonance stabilization of benzene, and the difference in energy between the ground state and the first excited state is so large that absorption occurs in the ultraviolet. In the case of fulvene the dominant structure in the ground state is (A), while the first excited state is stabilized by resonance among ionic structures such as (B); fulvene therefore absorbs in the visible region and is yellow in color. Cyclooctatetraene[118, 120] has a resonance energy of 12, while benzene has 41; the former absorbs at longer wave length. The lower resonance energy of cyclooctatetraene may be due to the ring being puckered or to the reduction of strain

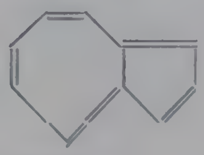
Fulvene



(A)



(B)


Azulene

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[28] See p. 334.
[84] See p. 371.
[85] See p. 371.
[119] P. and R. Daudel, *J. Chem. Phys.* **16,** 639 (1948).
[118] See p. 391.
[120] Prosen, Johnson, and Rossini, *JACS* **69,** 2068 (1947).

in the excited state. Similar considerations apply to azulene,[121] which is blue and which has a resonance energy of 46 in comparison with 77 for naphthalene.

Aromatic heterocyclics. Although heterocyclic systems are present in numerous dyes, information regarding their spectra is meagre.[122] Braude[35] has tabulated the available data (Table VI).

TABLE VI

ABSORPTION CHARACTERISTICS OF HETEROCYCLIC SYSTEMS

	λ'_{max} A.	ε'_{max}	λ_{max} A.	ε_{max}
Pyrrole	~2100	15,000	2400	300
Furan	~2000	10,000	2500f	1
Thiophene	—	—	2350	4500
Iminazole	<2100	>5000		
Thiazole	—	—	2400	4000
Indole	2150	25,000	2650f	6300
Thionaphthene	2250	30,000	2600f	10,000
Carbazole	—	—	2420	24,000
			2910	19,000
Diphenylene oxide	—	—	2500f	20,000
			2800f	16,000
Pyridine	1950	7500	2500f	2000
Pyrimidine	—	—	2450f	3000
Quinoline			2750f	4500
			3110f	6300
*iso*Quinoline			2620f	2300
			3180f	3200
1,2,3-Benztriazole			2760f	4500
Acridine	2500	160,000	3600f	1000
Phenazine	2500	120,000	3700	1600

NOTE: 'f' refers to a band showing fine structure.

Heterocyclic systems in which a nitrogen atom has replaced a methine group are similar in their absorption spectra to the hydrocarbon. The intensities are somewhat greater for the nitrogen heterocyclics, but the difference is not marked. The larger polarizability of the azomethine in comparison with the ethylene linkage, indicated for instance by the bathochromic shift in passing from stilbene to benzalaniline, thus plays a minor role in the cyclic resonators.

Shifrin[123] has calculated the wave lengths of the first absorption bands of pyridine, quinoline, acridine and phenazine on the assumption that a nitrogen atom in a heterocyclic molecule is analogous to a CH group and contributes one π-electron. Maccoll[124] has questioned this treatment of nitrogen atoms as equivalent to CH groups from a study of the gaseous absorption spectra of benzene, pyridine, and pyrimidine in which there is a bathochromic shift by the progressive replacement of CH by N.

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[121] Heilbronner and Wieland, *Helv. Chim. Acta* **30**, 953 (1947). See also Mann, Platt, and Klevens, *J. Chem. Phys.* **17**, 481 (1949).

[122] See, however, Cavalieri *et al.*, *JACS* **70**, 3875 (1948); Steck, Ewing, *et al.*, *ibid.* 3410, and earlier papers; *ibid.* **69**, 801 (1947); *ibid.* **70**, 2818 (1948).

[35] See p. 341.

[123] *Compt. rend. acad. sci. U.R.S.S.* **29**, 27 (1940).

Quantum-mechanical treatment of the absorption of unsymmetrical cyanines. Brooker's data have been submitted to quantum-mechanical treatment by Sklar,[125] who has derived an equation in agreement with the generalizations found empirically.

If e_1 and e_2 are the energy levels of the extreme structures of an unsymmetrical cyanine, the nondegeneracy is represented by $e_1 - e_2$. If the transition energies of the two related symmetrical cyanines are $\alpha\sigma N_1$ and $\alpha\sigma N_2$, the calculated mean is $(\alpha\sigma N_1 + \alpha\sigma N_2)/2$. Using a number of approximations, the transition energy of the unsymmetrical cyanine, ΔE_N, corresponding to the observed absorption, is given by the equation (2):

$$2\Delta E_N = \left[(e_1-e_2)^2 + (\alpha\sigma N_1)^2\right]^{\frac{1}{2}} + \left[(e_1-e_2)^2 + (\alpha\sigma N_2)^2\right]^{\frac{1}{2}} \qquad (2)$$

The Brooker deviation, expressed as frequency, should be proportional to the difference between ΔE_N and $(\alpha\sigma N_1 + \alpha\sigma N_2)/2$. The equation indicates three relationships which agree with the experimental findings. (1) The term $(e_1 - e_2)^2$ is positive, and the observed frequency of absorption should always be higher than the calculated frequency; i.e., the deviation should always be towards shorter wave lengths. (2) The term $(e_1 - e_2)^2$ will increase as the nondegeneracy of the extreme structures increases; the deviation should therefore increase with increasing asymmetry of the molecule. (3) In a vinylene homologous series of unsymmetrical cyanines such as (IX), $(e_1 - e_2)$ may be regarded as constant for all values of n; but the terms $\alpha\sigma N_1$ and $\alpha\sigma N_2$ diminish with n, and therefore the deviation should increase as the chain length increases. (4) The equation also affords an explanation of the "sensitivity rule." This follows from the fact that the resonance interactions $\alpha\sigma$ and the energy difference $e_1 - e_2$ enter into the transition energy as the square root of the sum of squares. When the difference $e_1 - e_2$ is small compared with the $\alpha\sigma$ terms a given increase in $e_1 - e_2$ affects ΔE_N much less than the same increase if $e_1 - e_2$ is of the same order of magnitude as $\alpha\sigma$ or larger.

The relationship is also illustrated in Fig. 27 taken from Herzfeld and Sklar's paper,[125] in which the transition energy is plotted against $e_1 - e_2$ for fixed values of $\alpha\sigma N_1$ and $\alpha\sigma N_2$ (these were taken to be equal in drawing the figure). It is clear that, because of the quadratic relationship, the effect on the transition energy of increasing e_1-e_2 by an amount Δe is very much less when e_1-e_2 is zero or small than when it is already appreciable.

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[124] *JCS* 670 (1946).

[125] *J. Chem. Phys.* **10**, 521 (1942); Herzfeld and Sklar, *Revs. Modern Phys.* **14**, 294 (1942).

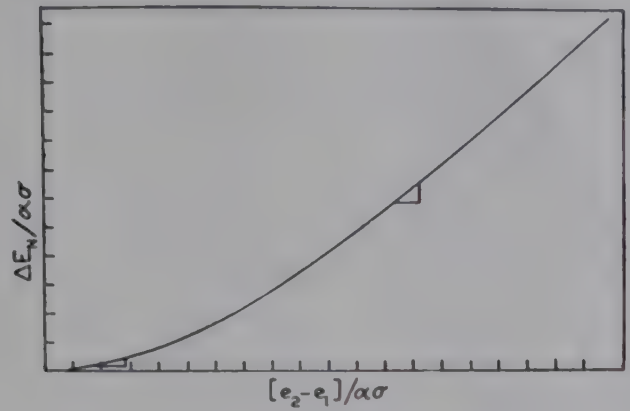

Fig. 27. Dependence of the transition energy, ΔE_N, on the energy difference, e_1-e_2. Each scale division represents one-tenth. The abscissae run from 0 to 1.9, the ordinates from 1.0 to 2.2 (Herzfeld and Sklar).

Quantum-mechanical calculations for idealized systems. Quantum-mechanical calculations have been made by Förster[126] for two models. One was an odd-membered conjugated chain of CH groups with auxochrome groups such as NH_2 or OH at both ends, represented by the cyanines. The other was similar but with a branched chain in the middle, represented by $(CPh_3)^+$ and its mono-, di- and trisubstituted derivatives. For both models absorption was displaced towards longer wave length with increasing length of chain and strength of auxochrome group in agreement with known properties of colored compounds. A theoretical substitution rule is deduced, stating that the absorption range of an unsubstituted ion breaks into two regions, one of shorter and the other of longer wave length, when the first auxochromic group is substituted. When the second auxochromic group is substituted both regions are shifted to longer wave lengths, and when the third is substituted the two regions merge into one of intermediate wave length. The models appear to be suitable as a starting point for calculations on more complicated systems.

Bayliss[127, 128] has proposed a "metallic" model for the spectra of conjugated polyenes. The π-electrons belonging to the double bonds of *trans*-conjugated polyenes are assumed to be a one-dimensional electron gas in a field of uniform potential energy whose length is approximately that of the conjugated system. The energy levels, the selection rule (Δn odd), and the transition intensities are deduced. The model predicts that the oscillator strength of the main absorption band of a *trans*-conjugated polyene is given by $f = 0.134\ (2N + 1)$ where N is the number of double bonds. The calculated values are in good agreement with experimental data. Unlike the bond orbital and molecular orbital treatments, this treatment does not require empirical parameters. Kuhn[129] has criticized the free-electron model in its application to the polyenes, but finds that it is an appropriate approximation for a number of other colored molecules, such as symmetrical carbocyanines, in which the two resonating structures of the cation are equivalent. He has shown that the position of the absorption maxima of symmetrical polymethines, Michler's hydrol blue and its derivatives, Malachite Green and other triphenylmethane dyes can be calculated by adopting a model of the dye molecule analogous to the free-electron gas model for metals. Porphyrines and phthalocyanines have been treated similarly. On the basis of this model Kuhn has also calculated the oscillator strength and the intensity of the first absorption band.

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[126] *Z. Physik. Chem.* **B47,** 245 (1940); *Z. Elektrochem.* **47,** 52 (1941).

[127] *J. Chem. Phys.* **16,** 287 (1948); **17,** 1353 (1949).

[128] See Platt, *ibid.* **17,** 484 (1949), for the use of a free-electron gas model in the treatment of the polyacenes.

INTENSITIES OF ABSORPTION BANDS

The problem of the intensities of absorption bands in relation to the structure of the absorbing molecule is even more complex than the frequency relationships, and there has been much greater success in correlating absorption frequencies with structural changes. The intensities of the absorption bands, as well as their wave lengths, are associated with the resonance states of the molecule, but the quantitative relationships are still largely obscure. While the wave length of an absorption band depends on the energy increment involved in the electronic transition with which the light absorption is associated, the intensity of the absorption depends on the probability of the transition. In butadiene the intensity per double bond is greater than in ethylene, and there is in general an increase in intensity as the length of the conjugate chain increases. High intensity has been related theoretically to the effect of structures (such as I) with large dipole

$$\overset{+}{C}H_2—CH=CH—\overset{\cdot\cdot\,-}{C}H_2 \qquad \text{(I)}$$

moments,[130, 131] which make the major contributions to the first excited state.

An ionic charge, which occupies different positions in the important resonance structures which can be formulated for a system as in the cations of basic dyes such as Malachite Green, Crystal Violet, and Methylene Blue, has been shown to be associated with intense absorption. Pauling[132] has deduced theoretically that this intensity of absorption is due to the marked difference in the distribution of charge in the various structures.

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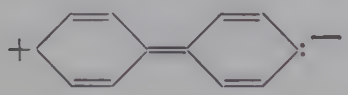
[129] *J. Chem. Phys.* **16,** 840 (1948); **17,** 1198 (1949); *Helv. Chim. Acta* **31,** 1441 (1948). See also Simpson, *J. Chem. Phys.* **16,** 1124 (1948); **17,** 1218 (1949).

[130] Mulliken, *J. Chem. Phys.* **7,** 121 (1939).

[131] *Reports on Progress in Physics* **8,** 231 (1941).

The intensity of absorption is greater per benzene ring in diphenyl than in benzene, and it increases in the order benzene < naphthalene < anthracene, etc. The intensity of an absorption band is related to the "allowability" of a transition. If "forbidden" transitions become "partly allowed," the absorption is very weak. This is the case with the transition associated with the 2,600A. band of benzene which becomes partly allowed through the distortion of the exact hexagonal symmetry of the electronic orbitals by the vibrational excitation of the carbon skeleton of the ring. Rodebush[93] and others have shown that when there is a steric inhibition of resonance in diphenyls by *ortho*-substitution, the effect on the absorption spectra is that the decrease in the intensity is much more pronounced than the change in the wave length of maximum absorption. Mulliken[133] has explained this observation. The first absorption band of diphenyl, which is of high intensity, is probably due to a transition to an excited state that results from resonance principally among ionic structures such as (II). The first absorption band of benzene, which is of low intensity, is due to a transition to an excited state that mainly results from resonance between the Kekulé structures. In the nonplanar diphenyls, ionic structures such as (II) are less stable than in diphenyl itself. The absorption is displaced towards shorter wave lengths; however, since the benzene rings are no longer effectively conjugated with each other, they now give rise to their normal absorption which, as in benzene, occurs at about the same wave length as in diphenyl, but is of considerably lower intensity.



(II)

Chako[134] and Förster[115, 135] have attempted to calculate the intensity and width of absorption bands from theoretical considerations. In terms of the classical theory of the light absorption process, Chako arrived at a relationship between the half-width of an absorption band (the distance between the points in the curve at which $\varepsilon = 1/2\ \varepsilon_{\text{max}}$), the frequency ($\nu_j$), the "oscillator strength" (f_j), and a quantity (γ_j) which is a measure of the damping responsible for the width of the band. In classical theory (f_j) is the number of electrons in a molecule which produce the band of absorption, and in quantum theory it represents the probability of the transition. Absorption bands in the visible and ultraviolet region are weak in comparison with those in the far ultraviolet with which the refractive index is associated. It follows from the theory of dispersion, e being the charge and m the mass of an electron, that

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[132] Gilman's Organic Chemistry, II, 2nd ed., Chapter 26, Wiley, New York, 1943.

[93] See p. 376.

[133] Quoted in Ref. 28.

[134] *J. Chem. Phys.* **2,** 644 (1934).

[115] See p. 390.

[135] See also ref. 20 and Morton, *Annual Repts. Chem. Soc. London* **38,** 7 (1941).

$$2n^2k=\frac{e^2}{\pi m}N'\frac{f_j\gamma_j\nu}{(\nu_j^2-\nu^2)^2+\gamma_j^2\nu^2} \qquad (1)$$

With $\varepsilon=4\pi nk/\lambda$ and $N'=N\mu$ (μ=molecules/cc.)

$$\varepsilon=\frac{2e^2}{cm}\,\frac{N}{n}\,\frac{f_j\gamma_j\nu^2}{(\nu_j^2-\nu^2)^2+\gamma_j^2\nu^2} \qquad (2)$$

For a narrow band, $\int\varepsilon\cdot d\nu=\frac{\pi e^2}{cm\nu_j^2}\cdot\frac{N}{n}\cdot f_j$, which is independent of γ. (3)

It then follows that

$$\varepsilon_{\text{max}}=\frac{2e^2N}{cm\nu}\cdot\frac{f_j}{\nu^2}\cdot\frac{1}{\gamma_j}\ (\nu=\nu_j) \qquad (4)$$

or

$$\gamma_j\cdot\varepsilon_{\text{max}}=\frac{2}{\pi}\int\varepsilon\cdot d\nu \qquad (5)$$

If γ is independent of ν throughout the band, the half-width is $\Delta\nu=2\gamma$. These equations apply to the gaseous state, and the intensity being measured in solution, a correction has to be applied to the measured intensity for obtaining the value for the gaseous state. Chako concluded that the influence of the solvent could not be accounted for by taking into account the Lorentz-Lorenz forces acting on the absorbing molecule due to the polarization of surrounding molecules. Mulliken and Rieke[131] have suggested that the refractive index of the solvent may be assumed to be 1, and no correction applied. From equation (1), and assuming that one electron per molecule is involved in the absorption and the half-width is $\sim 2{,}000$ cm^{-1}, ε_{max} works out to $\sim 10^5$. This is the upper limit of observed values for absorption in the visible and near ultraviolet, as well as the values indicated by quantum-mechanical calculations. For most substances ε_{max} is considerably smaller than this value. Braude[135a] has calculated the extinction coefficients for allowed transitions from considerations of the effective "chromophore area" and the polarization direction of the light absorbed; for polyenes and polycyclic benzenoid hydrocarbons, the calculated and observed values are in fair agreement.

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[131] See p. 396.

[135a] *JCS* 379 (1950); *Nature* **155**, 753 (1945).

Mulliken[130, 131, 136] has considered the quantum-mechanical aspects of absorption intensities, using the molecular orbital method. Most absorption bands in the visible or near ultraviolet may be characterized by transitions from a normal or homopolar state (N) to an ionic excited state (V_1). In molecular orbital terms, the transitions arise from the transfer of a π-electron from a bonding molecular orbital to an antibonding one. The intensity of absorption is mainly associated with the longest wave length transition ($N \longrightarrow V_1$), although the degree of this concentration is dependent on molecular character. Examining the absorption spectra of the carotenoids from this point of view, Mulliken has concluded that "the more elongated the molecule, the more the intensity should be confined to the long wave length and the more intense should be the color." In the case of some of the simpler molecules, he has made quantum-mechanical calculations of the intensity of the absorption bands.[137]

Sklar[138] has calculated the intensities of the long wave length transitions in substituted benzenes by the antisymmetrical molecular orbital method. The inductive and resonance effects of substituent groups in the benzene ring and their relation to the auxochromic properties of the groups have been discussed earlier. Intensity changes are mainly due to resonance or electron migration effects. Thus the amino group in aniline, by virtue of its unshared pair of electrons, produces a marked increase in the intensity of the forbidden transition of benzene at 2,600A. When the amino group is converted into the anilinium ion, it no longer possesses the unshared electron pair, and its spectrum is nearly identical with that of benzene. Sklar's treatment has shown that a large auxochromic or intensification effect is produced by a group which has an unshared electron pair, a shortened bond linking it with the nucleus, and a low ionization potential.

The very weak band at about 2,900A. shown by carbonyl compounds has been considered to have its origin in the lone pairs of electrons of the oxygen atom; the transition of one of these electrons to the same level as an excited electron of the carbon-oxygen double bond (but with a smaller quantum of energy) has been called an $N \longrightarrow A$ transition[139] (the transfer of an electron from a non-bonding orbital localized on the oxygen atom to an anti-bonding orbital of π-type in the C=O bond). Using dipole

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[130] See p. 396.

[131] See p. 396.

[136] *J. Chem. Phys.* **7,** 14, 339, 570 (1939); **8,** 234 (1940).

[137] See also Platt and Klevens, *ibid.* **16,** 832 (1948); and earlier papers.

[138] *Ibid.* **7,** 984 (1939); **10,** 135 (1942).

[139] McMurry and Mulliken, *Proc. Natl. Acad. Sci. U.S.* **26,** 312 (1940); Walsh, *Proc. Roy. Soc. London* **A185,** 176 (1946).

moment or ionization potential data, the " carbonyl polarity " of molecules has been quantitatively determined and correlated with the position of absorption bands.[140]

It may be possible some day to calculate from quantum-mechanical principles the energy differences as well as other characteristics of the electronic transitions between ground and excited states of complicated dye molecules, so that both the wave lengths and the intensities of absorption bands may be precisely related to molecular structure. Meanwhile, the continued search for empirical relationships between structure and spectra is useful, especially if they can be stated quantitatively as in the case of the groups of dyes examined by Lewis and by Brooker. The quantum-mechanical treatment of simple molecules and a consideration of the resonance structures of complex dyes are two opposite methods of approach which have been pursued in recent years, and a complete theory of the color of organic molecules is gradually taking shape.

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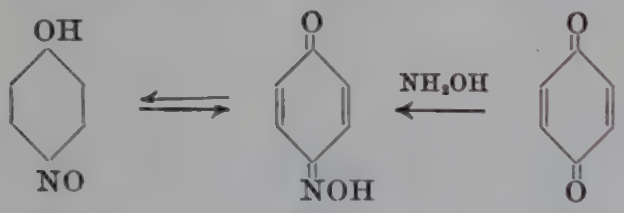
[140] Walsh, *Trans. Faraday Soc.* **43,** 158 (1947); See also McMurry, *J. Chem. Phys.* **10,** 655 (1942).

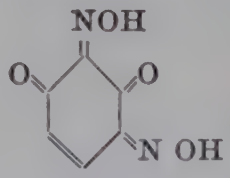
CHAPTER IX

NITROSO DYES

The nitroso dyes constitute a very small and technically unimportant group. On treatment with nitrous acid phenols and naphthols are readily nitrosated, and the nitroso compounds are tautomeric (I and II), as shown by the fact that they can also be prepared by the action of hydroxylamine on the corresponding quinones. Phenol is nitrosated in the *p*-position and *p*-nitrosophenol is an intermediate for indophenols.[1] *o*-Nitrosophenols form metal complexes and have mordant-dyeing properties. They are polygenetic dyes, that is, they yield differently colored complexes with different metals; but it is only the rather dull green iron lakes which have some interest in dyeing and printing.



(I) (II)



(III)

The affinity of *o*-nitrosophenols for some metallic ions is so strong that it is sufficient to shake a solution of the free *o*-nitrosophenol in petroleum ether with an aqueous salt solution to form immediately and quantitatively the corresponding nitrosophenol-metal complex.[2]

A reaction of theoretical interest is the simultaneous introduction of both the nitroso and hydroxyl groups into benzene by the combined action of the nitrosyl radical and an oxidizing agent. The nitrosyl radical is formed by reduction of nitrous acid or by oxidation of hydroxylamine, and the reaction is carried out in presence of a copper salt, which enables the *o*-compound to be exclusively formed.[3]

2,4-Dinitrosoresorcinol (III, Fitz, 1875) is readily obtained in nearly quantitative yield by addition of sulfuric acid to an ice-cold solution of resorcinol and sodium nitrite in water. It is best to use the freshly prepared substance as a 50% aqueous paste. The brownish-yellow compound is called Fast Green O (CI 1) since it dyes or prints green on an iron mordant, and it found considerable use at one time in calico printing. An interesting property of the substance is that on padding cotton with an alkaline solution and steaming, it combines with the cellulose (or perhaps polymerizes to a stable, insoluble compound) to yield a fast brown shade, and then acts as a mordant for basic dyes. The constitution of the iron lakes of (III) has been investigated by Morgan and Moss.[4, 5] An intense green lake was obtained when ferrous ammonium sulfate solution was added to an ammoniacal solution of (III); analysis of the lake and the reactions for ferric iron obtained on boiling the lake with concentrated hydrochloric acid showed that it was entirely the basic ferric compound (IV). The normal ferric lake (V) was obtained when ferric alum was used for lake formation.

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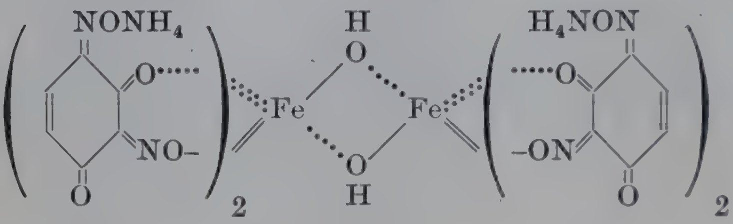
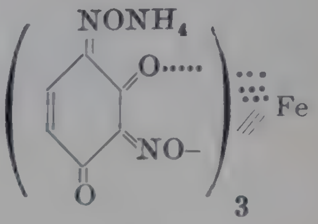
[1] See Chapters XXXV and XXXVI.

[2] Cronheim, *J. Org. Chem.* **12,** 1 (1947).

[3] Baudisch, *Naturwissenschaften* **27,** 769 (1939); *JACS* **63,** 622 (1941); *Arch. Biochem.* **5,** 401 (1944).



(IV)



(V)

The composition and properties of the cobaltammine and ferric lakes furnished evidence in support of the view that (III) contains one chelate group[5] and one salt-forming radical as indicated in (IV) and (V). The median isonitroso group alone is involved in the chelate complex, while the terminal isonitroso group behaves merely as an acidic radical.

Nitrosonaphthols. Nitrosation of α-naphthol gives a mixture of the 2- and 4-nitroso compounds. The former, Gambine R (CI 3), is the major product and it possesses mordant-dyeing properties, but is no longer used.

1-Nitroso-2-naphthol (VI; Fuchs, 1875; Gambine Y; Fast Printing Green; CI 2) prepared by adding sodium nitrite and then acid to a cooled solution of β-naphthol in aqueous caustic soda,[6] has been used as a dye for camouflage purposes in war because of the mellow shades resembling the tints of nature obtainable on various mordants (iron: green; chromium: brown; and zinc: yellow). The bisulfite compound is marketed as Pigment Green Salt for conversion into the green iron lake. If an aqueous solution of the bisulfite compound of (VI) is treated with ferrous sulfate and then with caustic soda, the ferrous lake, Pigment Green B (BASF, 1921; ST 2), is precipitated. Pigment Green B is obtained in fine texture suitable for filling rubber by suspending the bisulfite compound of (VI) in aqueous Turkey Red oil, and adding a mixture of ferric oxalate,

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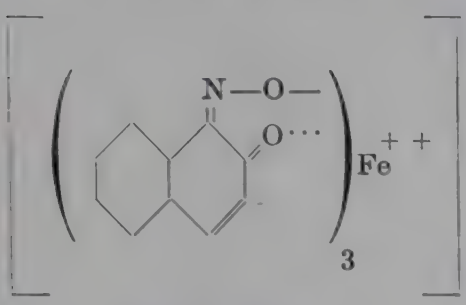
[4] *JCS* **121,** 2857 (1922).

[5] See also Chapter XIV.

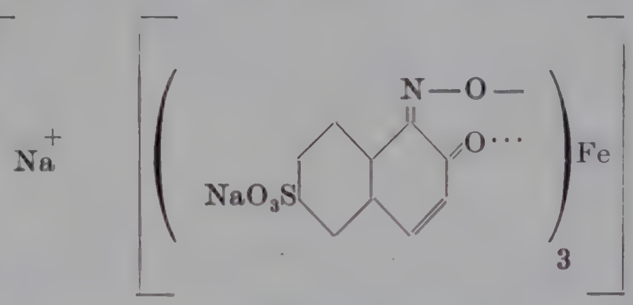
[6] *OSCV* I, p. 411.

oxalic acid and water, and precipitating by means of sodium carbonate.[7] Pigment Green 3B (BASF, 1919; ST 2N) is the iron complex of 1-nitroso-2-naphthol-3-carboxylic acid. Interaction of (VI) with sodium bisulfite and acidification gives 1-amino-2-naphthol-4-sulfonic acid, a largely used intermediate for mordant azo dyes. An interesting reaction of (VI), applicable also to 1-arylazo-2-naphthols, is its conversion by alkali cyanides into 1-amino-4-cyano-2-naphthol.[8]

1-Nitroso-2-naphthol-6-sulfonic acid (VII), prepared by nitrosation of Schaeffer's acid, is much more useful than the unsulfonated compound.



Pigment Green B



Naphthol Green B

It is marketed in the form of the soluble iron coordination complex, Naphthol Green B (Hoffmann, 1883; CI 5), produced by treatment of (VII) with ferric chloride. Naphthol Green B is of great interest, since it dyes as an acid color, being one of the fastest acid greens for wool; it was the first soluble dye containing coordinated metal and the forerunner of the metallized azo dyes of the Neolan type. The iron lake prepared by treating (VII) with ferrous sulfate, lime, and sodium carbonate is marketed as Pigment Green PLX (IG).[9]

Naphthol Green B is used for accelerating the solar evaporation of the water of the Dead Sea for the manufacture of common salt, potassium chloride, etc. Used in a concentration of 1 in 300,000, it effects the absorption of about 90% of the visible and infrared portion of sunlight.[9a]

The dark red precipitate which is formed quantitatively by the interaction of cobalt salts with (VI) in dilute acetic acid is useful for the detection and estimation of cobalt in presence of nickel. It has been stated[10] that 2-nitroso-1-naphthol is an even more sensitive reagent for cobalt. Colorimetric and photometric methods of estimation of iron[11] and cobalt[12] by means of nitroso-R-salt have also been suggested.

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[7] du Pont, USP 2,092,750.

[8] Bradley, Robinson, and ICI, BP 381,602.

[9] *BIOS* **961.**

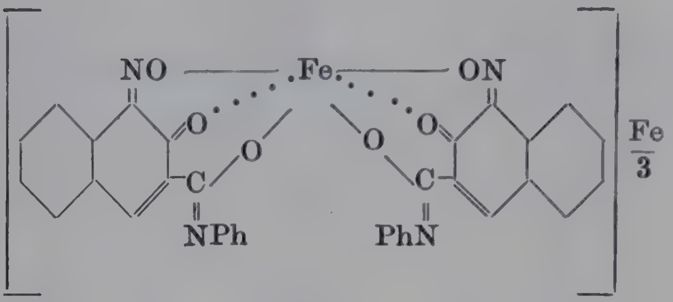
[9a] *Ind. Eng. Chem.* **42,** 7A (1950).

[10] Jung, Cardini, and Fuksman, *Anales assoc. quim. argentina,* **31,** 122 (1943).

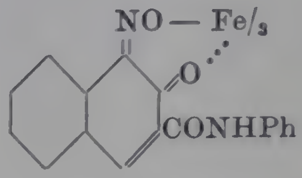
[11] Sideris, Young, and Chun, *Ind. Eng. Chem. Anal. ed.* **16,** 276 (1944).

[12] Haywood and Wood, *J. Soc. Chem. Ind.* **62,** 37 (1943); Willard and Kaufmann, *Anal. Chem.* **19,** 505 (1947).

Lakes of 1-nitroso derivatives of 2-hydroxy-3-naphthoic acid arylamides. Naphtol AS and its analogs,[13] when treated in alcoholic solution with different molecular proportions of ferric salt in presence of nitrous acid, yield two main types of iron complexes, which can be represented as (VIII) and (IX).[14] In the formation of the first type, enolization of the amide group is involved; this is confirmed by the fact that *N*-benzyl Naphtol AS gives only a lake of type (IX) even with excess ferric chloride. The pigments are bright green, and when used for coloring white Portland cement they exhibit excellent fastness to light and water.[15]

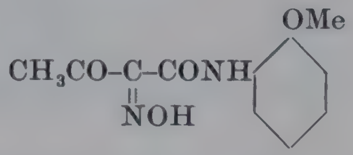


(VIII)



(IX)

The nitroso derivative (X) of acetoacet-*o*-anisidide forms a bluish green iron lake which is very fast to light; Fierz-David considers that demethylation precedes lake formation.[16]



(X)

When wool and silk are treated first with nitrites and then with metallic salts, *o*-nitrosation of the tyrosine residues and chelation with metal take place. Fast shades can be produced in this manner.[17]

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[13] See Chapter XXII.

[14] Kudva and Shah, unpublished work.

[15] Forster, Kudva, and Venkataraman, *J. Indian Chem. Soc. Ind. & News Ed.* **6**, 119 (1943).

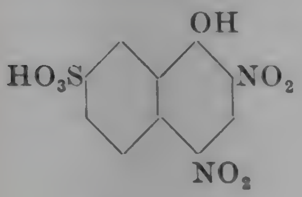
[16] Fierz-David, Künstliche Organische Farbstoffe, Ergänzungsband, Springer, Berlin, 1935, p. 11.

[17] Nilssen, Society of Dyers and Colourists Symposium on Fibrous Proteins, 1946, p. 142.

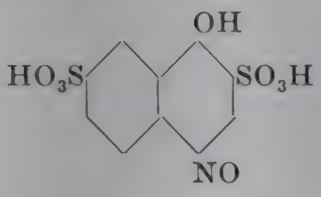
CHAPTER X

NITRO DYES

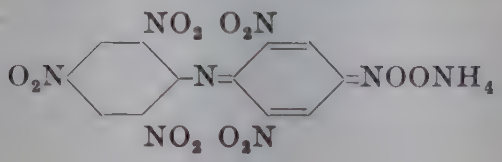
Nitro dyes are phenols or amines containing nitro groups in the *o*- and/or *p*-positions. The water-soluble members of the series are acid colors, and the insoluble compounds are useful pigments. Picric acid, the first synthetic dye, is no longer employed as a dye; picramic acid is an intermediate for mordant azo colors. The alkali salts of dinitrocresols were once used in dyeing and for coloring foods, but have been abandoned because of their toxicity. The value of picric acid and other nitrophenols as explosives is well known. Several nitrophenols have been suggested as antiseptics, weed destroyers, and insecticides,[1] examples being 3,5-dinitro-*o*-cresol as a fungicide, locusticide and rodenticide and 2,4-dinitro-1-naphthol (Martius Yellow; Manchester Yellow; Martius, 1864) as a moth-proofing agent. Manchester Yellow is poisonous and its use as a food color is prohibited. The only nitrophenol that continues to be used in dyeing is Naphthol Yellow S (Caro, 1879; CI 10), made by the action of nitrous acid on 1-naphthol-2,7-disulfonic acid, followed by treatment of the resultant 4-nitroso compound (I) with nitric acid. By the action of nitric acid on naphtholpolysulfonic acids only the sulfonic groups in the same ring as the hydroxyl are displaced by nitro groups. Naphthol Yellow S marketed as the sodium or potassium salt is a cheap dye for wool and silk, giving pure yellow shades; it can be used for greens by admixture with blues. It is also useful as a food color and for the preparation of lakes.



Naphthol Yellow S



(I)



Aurantia

The nitroamines are better dyes than the nitrophenols. The old leather dye, Aurantia (CI 12), the ammonium salt of hexanitrodiphenylamine obtained by nitration of diphenylamine, has become obsolete, being a skin irritant; but it has interest as an explosive.

Amido Yellow E (Schmidlin, 1911) (MLB; CI 11), prepared by the indicated series of reactions, is a wool dye which levels and exhausts well; the shades are moderately fast to light and washing but not to alkali.

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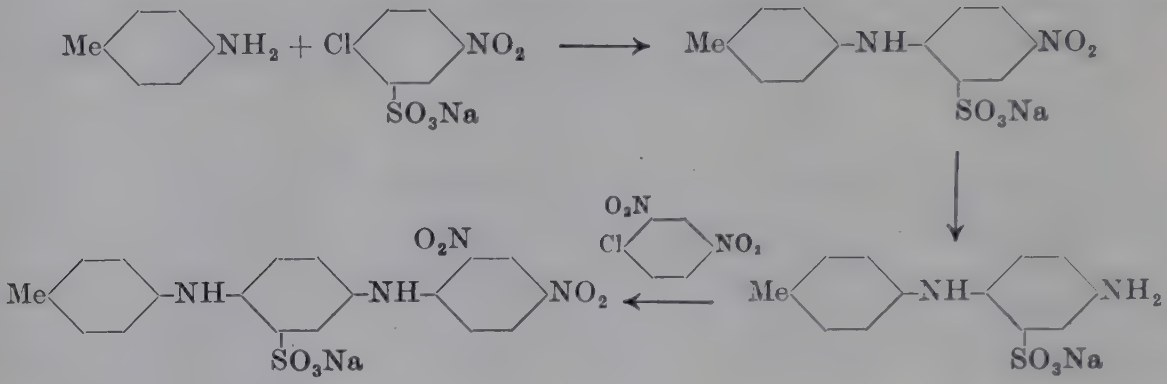
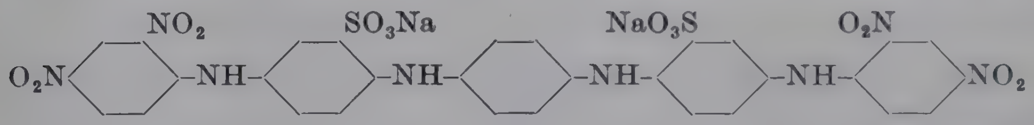
[1] Pastac, *Chimie et industrie* **51**, 49 (1944).

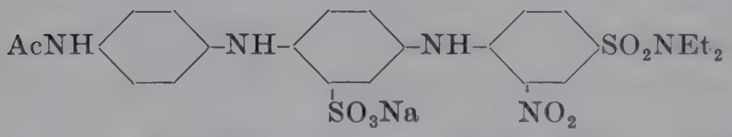
It would appear that later brands of Amido Yellow E did not have the methyl group, being prepared by condensation of 4-aminodiphenylamine-2-sulfonic acid with chlorodinitrobenzene. Faster dyes of the series are Polar Yellow Brown (Gy) and the brown wool and leather dye Anthralan Brown 4G (IG); Polar Yellow Brown is made by condensation of 4-chloronitrobenzene-3-sulfonic acid (2 moles) with *p*-phenylenediamine (1 mole), reduction to the diamine, and finally condensation of this diamine with two moles of 2,4-dinitrochlorobenzene. Anthralan Brown 4G is prepared by condensation of 4-amino-4′-acetamidodiphenylamine-2-sulfonic acid with 2-chloronitrobenzene-5-sulfondiethylamide;[2, 3] the influence of the acetamido group in imparting affinity and level dyeing character as a wool color is interesting, since Igenal Brown 3G, which is constituted as Anthralan Brown 4G but without the acetamido group, belongs to the Igenal (IG) range of leather dyes.



Amido Yellow E



Polar Yellow Brown



Anthralan Brown 4G

Among the insoluble coloring matters used as aqueous dispersions for dyeing cellulose acetate (see Chapter XXI), some of the early representatives were nitrodiphenylamines, which had good affinity for acetate silk and light fastness. Golden Yellow VIII (2,4-dinitro-4′-hydroxydiphenylamine)[4] and Golden Orange III (4-chloro-2-nitro-3′-ethoxydiphenylamine) are examples in the S.R.A. range of the British Celanese Co.[4] The nitrile (II) is rather weak tinctorially, but is interesting because of its good light fast-

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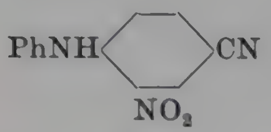
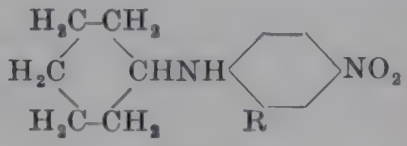
[2] IG, BP 451,183.

[3] *BIOS* 1548.

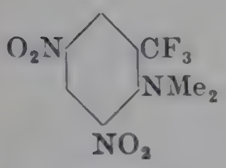
[4] Rowe, The Development of the Chemistry of Commercial Dyes, Institute of Chemistry, London, 1938.

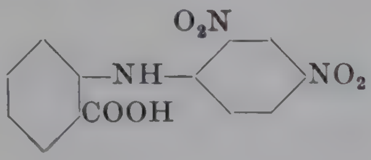
ness.[5] The cyclohexylamine derivative (III; R$=NO_2$) has been used.[6] Recent patents give evidence of continued interest in nitro dyes.[7] Nitroamines containing a trifluoromethyl group are yellow to orange dyes for acetate rayon; an example is (IV).[8] The products of the condensation of tetrahydroquinoline compounds with chloronitrobenzenes are dyes for wool, silk, and acetate rayon.[9]

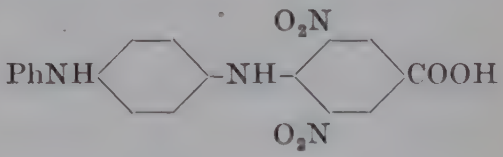

(II)

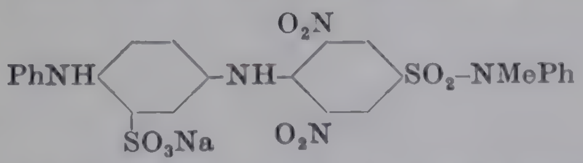

(III)

Nitrodiphenylamine derivatives (e.g. V) containing a carboxyl or sulfonic group yield aluminium and barium lakes with good fastness to light.[6] Carboxylic and sulfonic acids of nitro compounds are also useful as bright yellow to brown dyes for acetate silk, although the fastness to washing is low because of the strong acidity of the molecules (cf. Chapter XXI). Cellit Fast Brown R (IG)[10] is prepared by the reaction of *p*-aminodiphenylamine with 4-chloro-3,5-dinitrobenzoic acid; other examples of this type are (VI) and (III; R$=SO_3Na$). The last is prepared by condensing 4-chloronitrobenzene-3-sulfonic acid with cyclohexylamine, a useful intermediate for dyes of this type which have affinity for wool as well as cellulose acetate.[11] Introduction of a sulfonic group in Cellit Fast Brown R by use of 4-aminodiphenylamine-2-sulfonic acid leads to the useful wool dye Amido Naphthol


(IV)


(V)


Cellit Fast Brown R


(VI)

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[5] *FIAT* 1313.

[6] Fierz-David, Künstliche Organische Farbstoffe. Ergänzungsband, Springer, Berlin, 1935.

[7] E.g., see Eastman Kodak, USP 2,496,695; 2,470,095.

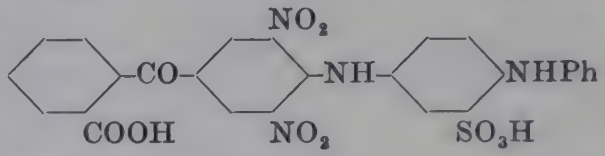
[8] Daudt, Woodward and du Pont, USP 2,212,825.

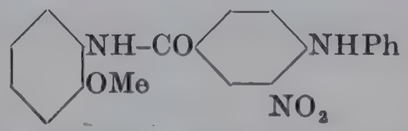
[9] Dickey, James, and Eastman Kodak, USP 2,251,922.

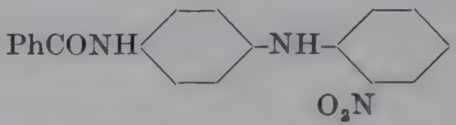
[10] Report 19, Textile Series, Office of the Quartermaster General, U.S. Dept. of Commerce.

[11] IG, DRP 507,831.

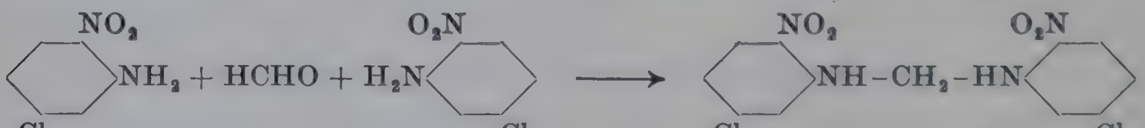
Brown 3G.[3] It has been stated that 2-nitro-4′-alkyldiphenylamine-4-sulfonic acids are light- and acid-fast yellow dyes.[12] Nitro dyes of the type (VII) containing a benzoylbenzoic acid group are brown dyes with good light fastness.[13] Nitrodiphenylaminecarboxylic amides (e.g. VIII) and esters are being claimed in recent patents for application to cellulose acetate as aqueous dispersions; the yellow shades are fast to light, washing, and steaming, and they leave cellulose and animal fibers undyed.[14] The compound (IX) dyes cellulose acetate a brilliant yellow.[15] The yellow diphenylamine dyes prepared by condensing primary aromatic amines with *o*-nitrochlorobenzene derivatives carrying a sulfamyl or hydrazinosulfamyl group are suitable for cellulose acetate, nylon, wool, and silk.[16]

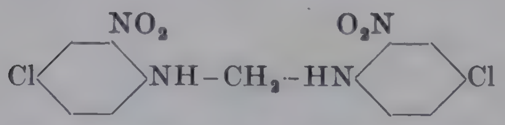

(VII)

(VIII)



(IX)

A few nitro coloring matters are used as pigments. Pigment Chlorine GG (Fussenegger, 1908; BASF; CI 13) and Lithol Fast Yellow GG (BASF; CI 14; Sirius Yellow GG) are prepared by condensing the appropriate chloronitroaniline with formaldehyde in presence of sulfuric acid.[17]


Pigment Chlorine GG


Lithol Fast Yellow GG

Nitro groups may be introduced in other chemical classes of dyes for modification or improvement in the dyeing and fastness properties. Orange IV is sensitive to (reddened by) acids, whereas nitration yields a mixture of nitro derivatives (Indian Yellow; Jasmin; Citronin) fast to acid. Other examples of useful azo dyes and azoic pigments containing nitro groups are quoted later. Alizarin Orange (3-nitroalizarin) was valued at one time for the brilliant orange it gave on aluminium mordant.

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[3] See p. 406.

[12] Seymour and Salvin, USP 2,443,666.

[13] Geigy, BP. 589,057.

[14] Olpin and Argyle, USP 2,368,723; BP 550,251.

[15] Argyle, USP 2,388,663.

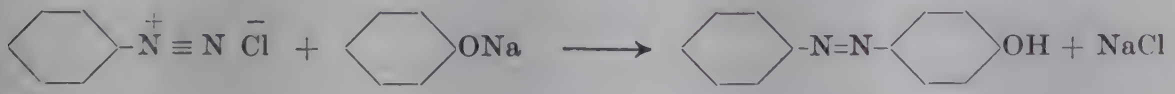
[16] McNally, Dickey, and Eastman Kodak, BP 585,940; Seymour *et al.*, USP 2,474,333.

[17] Rowe and Levin, *J. Soc. Dyers Colourists* **38**, 203 (1922).

CHAPTER XI

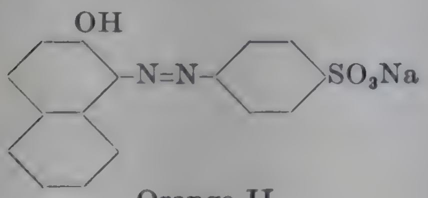
AZO DYES—GENERAL

Azo dyes, of which the commercial representatives probably amount to over a thousand inclusive of all types with the common feature of one or more azo groups, constitute numerically the most important class of the synthetic coloring matters; and in money value they are second only to the anthraquinonoid vat dyes. Over 50% of the dyes listed in the Color Index belong to the azo class, and the proportion of azo dyes has been stated variously as half to three-quarters of all the synthetic dyes now in use. The azo dyes are a distinct and clearly defined class, characterized by the presence of one or more azo (—N=N—) groups. They have no analogs among the natural coloring matters. They are all prepared by a common process involving two reactions: (1) diazotizing an aromatic primary amine;[1] and (2) coupling the diazonium salt with a phenol or aromatic amine with a free *o*- and/or *p*-position, or with certain other components having reactive positions, such as β-ketonic acid arylamides.[2] Diazotized aniline (benzenediazonium chloride) couples with phenol in alkaline solution to form *p*-hydroxyazobenzene (I).

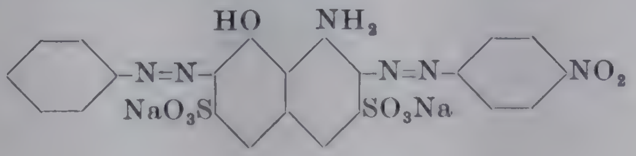


(I)

The amine which is diazotized (A) is the first component, and the substance with which it couples is the second or end component (E), and the reaction is indicated by the shorthand A⟶E. The scheme of preparation of Orange II for instance is simply and conveniently shown as (sulfanilic acid ⟶ β-naphthol).



Orange II



Naphthol Blue Black

This method of representing the final reaction or series of coupling reactions is especially useful for polyazo dyes, in which the order and pH of coupling can be readily understood. Thus the preparation of a disazo dye by coupling two different diazonium salts with a single second component like H-acid having two coupling positions is indicated as follows: ($A^1 \xrightarrow{\text{1. acid}}$ H-acid $\xleftarrow{\text{2. alk.}} A^2$). For many purposes the structural formula of a dye such as Naphthol Blue Black does not need to be written, since it is adequately shown by the scheme (*p*-nitroaniline $\xrightarrow{\text{1. acid}}$ H-acid $\xleftarrow{\text{2. alk.}}$ aniline). The numbers and terms (acid or alkali) adjoining the arrows show that A^1 was coupled first under acid conditions, and A^2 then coupled under alkaline conditions. An obviously important feature of the scheme for representing the preparation of azo dyes is that it immediately indicates the intermediates from which a dye is prepared. The color and dyeing properties of an azo dye are determined by the nature of the intermediates and the manner in which they are linked together, and both are apparent from this scheme.

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[1] See Chapter IV.

[2] See Chapters XII–XXII for numerous examples of coupling components and conditions.

Since diazonium coupling is a general reaction, wide variations are possible in the choice of components, and in the color and dyeing properties of the dyes produced. Until recently there was a lack of greens in certain ranges, but the azo series now comprise dyes of all shades, with the exception that bright green acid colors for dyeing wool directly are still not available. Azo dyes are adaptable to a wider variety of applications than any other group of dyes. They are applicable to all the natural and synthetic fibers, and the group includes direct or substantive cotton colors, acid colors, mordant dyes (metallizable in substance or on the fiber), and insoluble dyes, which may be used as pigments or prepared on the fiber by an ingrain or *in situ* method. By the use of basic components basic azo dyes can be prepared, although these are not so important as the triphenylmethane or other groups of basic colors. Many dyes applicable to paper, leather, rubber, and other materials belong to the azo class. Certain azo dyes in specially pure form are used for coloring foodstuffs. Minor uses of azo dyes are as indicators, drugs and stains in bacteriological and histological work. The azo pigments or insoluble azo compounds, and the lakes prepared by the combination of azo dyes and metallic salts are valuable in the paint, varnish, lacquer, and allied industries.

Azo dyes are made from a large range of intermediates, which often involve a long series of reactions and a great variety of plant, some of considerable complexity; but the plant[3, 4] for the diazotization and coupling reactions merely consists of wooden vats provided with mechanical agitation. The vats may be lined with rubber or tiles, and they are arranged in tiers so that the diazonium solution can be dropped into the coupling solution by gravity, and a second and third coupling may be carried out if necessary. Large quantities of ice and common salt are

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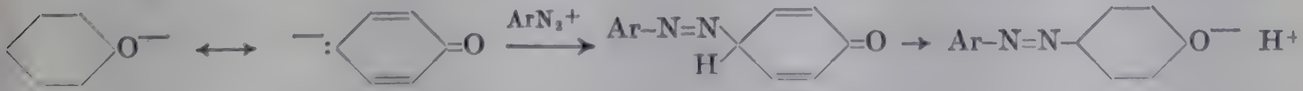
[3, 4] For accounts of IG manufacturing processes and plant for azo dyestuffs, see *BIOS* (3) **961**; (4) **1548**.

consumed in azo dye manufacture, and it is usual to have an ice plant and ice crusher in the azo shed and to provide chutes through which ice and salt can be delivered to the vats. Filter-presses, dryers, and the equipment required with all dyes for mixing and grinding to produce the commercial brands in standardized qualities complete the plant. Given intermediates of the requisite purity, the main factors in a successful coupling process, which sometimes proceeds quantitatively, are the control of temperature and pH, and the precipitation of the dye by salting out in a readily filterable form. Azo dyes are standardized by mixing with common salt or calcined Glauber's salt. Typical processes for azo dyes are described in Chapter XII for Metanil Yellow, Orange II, and Naphthol Blue Black.

THE COUPLING REACTION

The effective agent in a smooth and rapid diazonium coupling is the positively polarized diazonium radical ArN_2^+, which is strongly electrophilic and attacks anionoid or nucleophilic centers, such as the *o*- and *p*-positions in sodium phenolate or aniline. The mechanism of the reaction between diazonium salts and aromatic phenols or amines has not yet been completely elucidated, and there have been differences in the interpretation of the known facts. Although numerous qualitative observations have been recorded regarding the behavior of various diazotized amines towards various phenols and amines, and a kinetic study has been made in a few cases,[5, 6] it will be of interest to obtain more extensive data on the coupling of components of definite and progressive variations in structure. The present knowledge is sufficient, however, to indicate that the diazonium coupling reaction is explicable by a mechanism which is in consonance with the accepted theory of aromatic substitution.

Phenols are coupled in alkaline solution with diazonium salts. The alkaline reaction of aqueous solutions of the diazonium carbonates, the electrical conductivity of solutions of diazonium salts, and other properties[1] have shown that diazonium compounds are ionized in aqueous solution. In the phenoxide ion (I) the 4-position is a site of high electron density, and the diazonium coupling reaction consists essentially in the attack of this electronegative site by the positively polarized or cationoid diazonium radical. Repulsion of a proton from the activated complex (II) then takes place and the formation of the azo compound is completed.



(I) (II)

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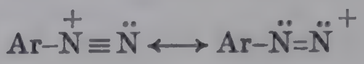
[5] Cf. Conant and Peterson, *JACS* **52**, 1220 (1930).

[6] Wistar and Bartlett, *ibid.* **63**, 413 (1941).

[1] See p. 409.

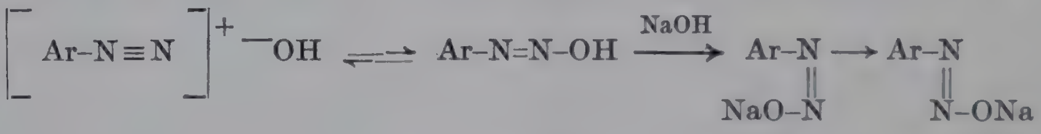
The diazonium ion may be represented by two resonance structures (IIIA) and (IIIB), of which (IIIA) makes the main contribution on account of its stability, but it may be the unstable structure (IIIB), having a nitrogen atom with a sextet of electrons, which enables the attachment to the anionoid carbon atom in the phenoxide ion to take place[7] with the formation of the azo linkage Ar-N=N-Ar′.



$$\mathrm{Ar{-}\overset{+}{N}{\equiv}\ddot{N} \longleftrightarrow Ar{-}\ddot{N}{=}\ddot{N}^{+}}$$

(IIIA) (IIIB)

The diazonium ion (III) reacts reversibly in water to form the aryldiazohydroxide (IV), which exists in stereoisomeric forms and is a weak acid. In strongly alkaline solution the acid forms the diazotates (VA and VB), and the equilibrium between the ion (III), which is the effective coupling agent, and the diazohydroxide (IV) will depend on the nature of the aryl group and the pH of the medium. Although diazonium salts are in general unstable at the pH of coupling, and both (III) and (IV) can undergo various decompositions,[1] a normal coupling reaction frequently proceeds so rapidly at low temperature that it is completed before any noticeable decomposition of the diazonium salt takes place. It is necessary to have the alkali in slight excess to keep the phenol in solution as the sodium salt; but a large excess of alkali will tend to slow down the coupling as a result of the formation of the *anti*-diazotate (VB), which is devoid of coupling power. A pH range of 7–9 is suitable and in technical practice couplings are usually carried out in sodium carbonate solution. With a given diazonium salt and within limits depending on the acidity of the phenol, the rate of coupling increases with the pH, for the availability of the phenoxide ion is the determining factor.



$$\left[\mathrm{Ar{-}N{\equiv}N}\right]^{+}\,{}^{-}\mathrm{OH} \rightleftharpoons \mathrm{Ar{-}N{=}N{-}OH} \xrightarrow{\mathrm{NaOH}} \begin{matrix}\mathrm{Ar{-}N}\\ \|\\ \mathrm{NaO{-}N}\end{matrix} \longrightarrow \begin{matrix}\mathrm{Ar{-}N}\\ \|\\ \mathrm{N{-}ONa}\end{matrix}$$

(III) (IV) (VA) (VB)

The yield in a coupling reaction depends on the electrochemical character of the diazonium group, as determined by the inductive and resonance effects of the nuclear substituents; on the electronegativity and accessibility of the site in the phenol or naphthol at which the attachment of the diazonium group is to take place; and on the pH of the reaction mixture. Many examples of diazonium salts of varying coupling energy and of second components which couple with varying ease are quoted in the sequel. When the coupling components are a weakly polarized diazonium salt and a second component in which the coupling position does not possess adequate electronegativity, coupling will proceed very slowly or not at all. On the other hand, when the coupling components are a powerful diazonium cation and a phenol in which the *o*- or *p*-position is a site of high electron density, coupling is as rapid as ionic reactions or inorganic double decompositions.

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[7] Hauser and Breslow, *ibid.* **63**, 418 (1941).

[1] See p. 409.

Conant and Peterson[5] found that the coupling of diazotized sulfanilic acid, *p*-bromoaniline, aniline, *p*-toluidine or *o*-anisidine with naphtholsulfonic acids at pH 4.5 to 9.15 is bimolecular and that the rate of coupling is a simple function of the hydrogen ion activity of the buffer solutions.

In general, diazonium salts of negatively substituted amines, such as the nitroanilines, nitrochloroanilines, and the anilinesulfonic acids couple more rapidly owing to the inductive and resonance effects of the nuclear substituents.[8] The nitro group is especially effective on account of the positive polarization of the nitrogen atom, which withdraws electrons from the ring and increases the positive charge on the diazonium ion. When the nitro group is in the *o*- or *p*-position, the resonance effect further enhances the positive charge on the diazonium group, which may then be regarded as not merely cationoid in character but as a definite and powerful cation.[9] Nuclear halogen atoms, owing to their strongly electronegative character, have an inductive effect in the same sense, but since any resonance effect functions in the opposite direction the influence of halogen atoms on coupling is of a minor order in comparison with nitro groups. Diazotized 2,4-dinitroaniline is more reactive, or possesses higher coupling energy than *o*- and *p*-nitrobenzenediazonium chloride; diazotized 2,4,6-trinitroaniline has still higher coupling energy and is able to couple with the hydrocarbon mesitylene. The diazonium salts of *p*-nitroaniline and similar negatively substituted amines couple with β-naphthol (and with anisole) even under strongly acid conditions, for instance in a medium of concentrated sulfuric acid and phosphoric acid.[10]

The relative rates of coupling for the diazonium salts of aniline and certain *p*-substituted derivatives are: NO_2, 1300; SO_3^-, 13; Br, 13; none, 1; CH_3, 0.4; CH_3O, 0.1. Using one of five different phenolic second components, Conant and Peterson found that the relative rates of coupling of the various diazonium salts were the same within about 25%.

In the coupling of a tetrazotized diamine such as benzidine, one diazonium group couples rapidly, and the second then more slowly. Tetrazotized *p*-phenylenediamine also couples in two definite stages; one of the diazonium groups is so strongly polarized that, like the diazonium salts of the nitroanilines, it couples with β-naphthol or anisole in sulfuric acid solution.[10] This is doubtless due to the inductive effect of one diazonium group on the other as in (VI), so that one of the groups (A) acquires an increased positive charge which enables it to couple with the nonionized β-naphthol molecule. Once a monoazo dye (e.g. VII) is formed, the positive charge at (B) is diminished by the resonance effect indicated in the structure (VII), which will then couple only under favorable conditions; it will couple for instance with alkaline β-naphthol, but more slowly than diazotized aniline. Coupling tetrazotized *p*-phenylenediamine with β-naphthol methyl ether in sulfuric acid solution, Schoutissen[10] found that coupling was accompanied by demethylation.

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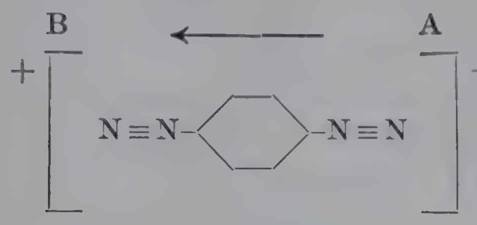
[5] See p. 411.

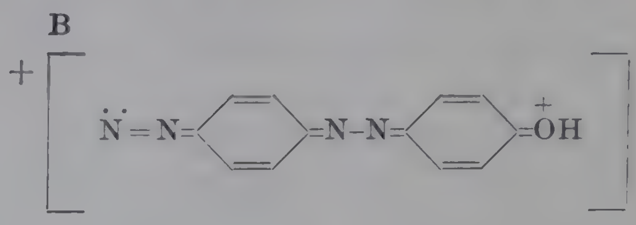
[8] See Chapter VIII.

[9] See also Poraî-Koshits and Grachev, *J. Gen. Chem. U.S.S.R.* **16**, 571 (1946); Burmistrov, *ibid.* **18**, 1361 (1948).

[10] Schoutissen, *JACS* **55**, 4541 (1933).

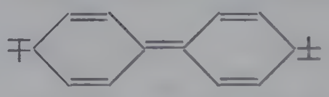


(VI)



(VII)

The behavior of tetrazotized benzidine is analogous to that of tetrazotized *p*-phenylenediamine so far as the greater reactivity of one diazonium group is concerned; it is well known that, in the preparation of disazo dyes from benzidine, the second coupling takes place much more slowly than the first. However, the small but appreciable contribution made by the structure (VIII) to the resonance of diphenyl diminishes the electrophilic inductive effect of one diazonium group on the other, so that the increase in the positive charge of the other diazonium group is not large enough, as in the case of tetrazotized *p*-phenylenediamine, for coupling with nonionized β-naphthol in acid solution to take place.



(VIII)

Coupling positions. The position of attachment of an azo group to a carbon atom in a coupling reaction is governed by a general rule, which follows from the mechanism of the reaction. The diazonium group attacks a position which has been activated as a site of high electron density. Coupling therefore takes place in the *o*- or *p*-position to the directing hydroxyl or amino group in the second component; if both these positions are occupied no coupling will take place, or one of the substituents will be displaced. Coupling never takes place in the *m*-position to the directing group.

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[10] See p. 413.

Coupling with phenol and its derivatives. As between the *o*- and *p*-positions, both of which are sites of high electron density, the *para* is much more favored, and in this respect diazonium coupling is distinct from nitration and other reactions of phenol in which both the *o*- and *p*-substituted compounds are formed. This indicates the significance of the mesomeric effect in the phenoxide ion, which tends to couple at the terminal carbon atom in a conjugated series of double bonds. With benzenediazonium chloride coupling occurs almost exclusively (in a yield of over 99%) in the *p*-position with the formation of *p*-hydroxyazobenzene; the *o*-compound is isolable by steam distillation. When the *p*-position is occupied, as in *p*-cresol, coupling takes place readily in the *o*-position; such *o*-coupling is in fact of much greater technical importance than *p*-coupling, since *o*-hydroxyazo dyes possess special and valuable tinctorial and dyeing properties. If the *p*- and both the *o*-positions are occupied, coupling will either not take place, or one of the groups will be replaced.

If both the *o*- and *p*-positions are free and 2 moles of the diazonium salt are used, the 2,4-disazo derivative can be prepared; with 3 moles or more of the diazonium salt, the 2,4,6-trisazo dye is also obtainable, but only in small quantities admixed with the disazo compound, since the third coupling takes place with considerable difficulty.

Sodium salicylate couples less readily than sodium phenolate because of internal hydrogen bond formation as well as the deactivating effect of the carboxyl ion; but the coupling is rapid enough for technical application and is used in the preparation of azo dyes with mordant dyeing properties; the fact that salicylic acid couples with one mole of a diazonium salt exclusively in the *p*-position to the hydroxyl is utilized in the preparation of 5-aminosalicylic acid. The advantage of this route is that nitration of salicylic acid gives a mixture of the 3- and 5-nitro derivatives which have to be separated and reduced.

Resorcinol is an important component in the preparation of azo dyes; resorcinol and *m*-phenylenediamine are the two benzene derivatives which are of value in the preparation of primary disazo dyes by the use of a single second component capable of dual coupling. Both resorcinol and *m*-phenylenediamine can in fact couple with 3 moles of the same or different diazonium salts although the third coupling usually does not proceed to completion; and useful dyes, particularly for leather, are thus obtainable.

The coupling of resorcinol with 1 mole of benzenediazonium chloride at a pH of about 7 gives 4-benzeneazoresorcinol; chromatography has shown the absence of the 2-azo compound. Resorcinol couples so readily that even with 1 mole of benzenediazonium chloride about 10% of a disazo dye is formed.[11] If coupling with 2 moles of diazonium component is carried out at pH 5–8, the main product is 2:4-bisbenzeneazoresorcinol. 4-Benzeneazoresorcinol (IX) is first formed, and the entry of the second azo group into the 2-position is due to the chelation indicated in (IX), as a result of which one of the Kekulé structures makes a larger contribution to the resonance of the benzene ring; coupling then takes place at the end of the double bond attached to the hydroxylated carbon atom. Under strongly alkaline conditions the hydrogen bond is broken, and coupling takes place, as in resorcinol itself, in the *o*,*p*-position to the two hydroxyl groups,[12] as indicated in (X).

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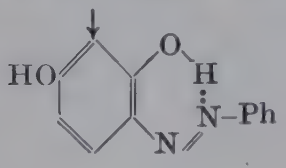
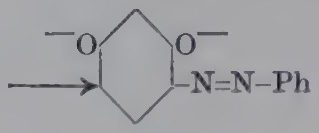
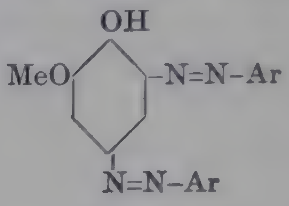
[11] Gore, unpublished work.



(IX)



(X)

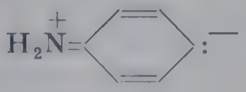


(XI)

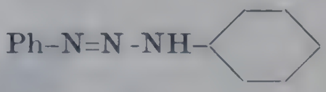
Resorcinol may be coupled in one operation or in progressive stages with 3 moles of a diazonium salt. The second coupling proceeds to completion very readily, but not the third. With diazotized aniline, the trisazo dye is obtained in about 25% yield; better yields of the trisazo dye can be obtained from diazonium salts of higher coupling energy, but the third coupling cannot be carried out quantitatively.[11]

Catechol couples slowly, whereas guaiacol undergoes facile coupling to form the monoazo or disazo compound (XI), depending on the proportion of diazonium salt employed. Hydroquinone reduces diazonium salts.

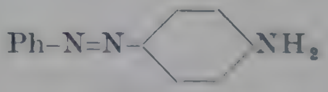
Coupling of aromatic amines. Aromatic amines couple with diazonium salts under neutral or weakly acid conditions (pH 4 to 7).[2] Below pH 6 the coupling slows down with increasing acidity, since the availability of the free amine determines the rate of coupling.[6] The diazo group enters the *p*-position when this is unoccupied, and otherwise the *o*-position, as may be expected from the resonance structures (e.g. I) of the free amine, comparable with the resonance of the phenoxide ion; but since these resonance contributions are much greater in the phenoxide ion where no separation of charge is involved, the activation of the *o*- and *p*-positions (especially the former) is less powerful in aniline, and amine couplings



(I)



(II)



(III)

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[12] Contrast Baker, *JCS* 1684 (**1934**); Hodgson and Marsden, *J. Soc. Dyers Colourists* **60**, 120 (1944).

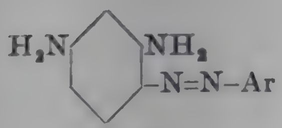
[11] See p. 415.

[2] See p. 409.

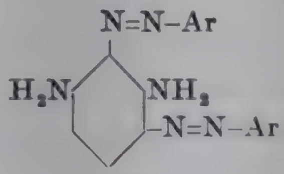
[6] See p. 411.

are markedly slower than alkaline phenol couplings. However, neutral amine coupling proceeds often more readily than the coupling of phenol in neutral solution because of the greater stability of the structure (I) in comparison with the analogous resonance structure of phenol. It has been suggested that the diazoamino compound (II) is usually formed first in the coupling of diazonium salts with primary and secondary amines, and then under acid conditions rearranges to the aminoazo compound (III). With the more reactive diazonium salts and the more reactive amines such as *m*-phenylenediamine and 2,5-dimethoxyaniline, the diazoamino compound, if formed, is immediately isomerized to the aminoazo compound. In the conversion of a diazoamino compound into the aminoazo compound, the formation of the free diazonium radical is an intermediate stage, as evidenced by the fact that in the presence of a coupling component more reactive than the amine residue (e.g. β-naphthol), the product is the azo dye derived from the naphthol; these facts are utilized in stabilizing diazonium salts as diazoamino compounds and using them in admixture with alkali naphtholates for azoic printing.

Diazonium salts are rapidly reduced by *o*- and *p*-phenylenediamine. *m*-Phenylenediamine couples smoothly, giving the 4-monoazo compounds (IV) or a mixture of the 2,4- and 4,6-disazo compounds (V) and (VI), according to the molar proportions of the diazonium salt. Dyes of both types are important and the second coupling may be carried out on the fiber. The constitution of disazo dyes from *m*-phenylenediamine has not been investigated, although certain dyes have been formulated (e.g. in the Colour Index) with 4,6-orientation of the azo groups, and others with the 2,4-orientation. From steric consideration it is probable that diazonium salts loaded with substituents couple in the 4,6-positions.



(IV)



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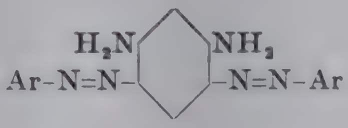

(VI)

m-Phenylenediamine derivatives substituted in the 4,6-positions couple weakly with diazonium salts to give poor yields of the 2-azo compound, the coupling apparently taking place through the intermediate formation of the diazoamino compound. On coupling 4,6-diamino-*m*-xylene (VII) with diazotized aniline, Morgan[13] found that the brownish-yellow precipitate frothed and evolved nitrogen, and finally became resinous; by extraction of the tarry precipitate with benzene a small amount of the azo dye could be isolated. On the other hand, 2,6-diamino-*m*-xylene (VIII) coupled readily because of the availability of the 4-position in the *m*-phenylenediamine residue.

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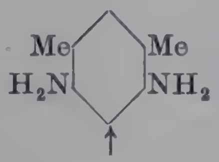
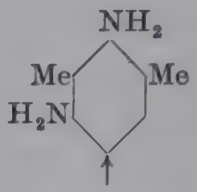
[13] *JCS* **81**, 83 (1902).

(VII)





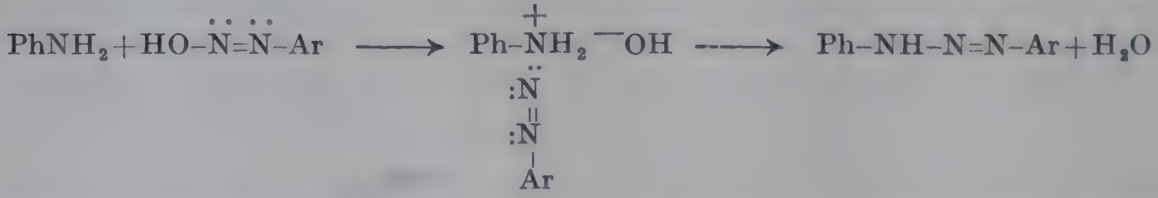
(VIII)

While the conditions that lead to the formation of diazoamino compounds (II) have to be carefully avoided in coupling primary and secondary amines with diazonium salts in order to obtain the aminoazo compounds (III), a tertiary amine, like dimethylaniline, is free from this complication. Karrer[14] found that in the coupling of dibutyl and diamylaniline with diazotized sulfanilic acid an alkyl group was split off. Hickinbottom and Lambert[15] have, however, shown that the tertiary amines examined by Karrer, as well as other tertiary amines with even larger alkyl groups, couple normally without displacement of an alkyl group.

Under neutral conditions the diazonium radical reacts reversibly to form the covalently bound diazo-acid (IX) which then undergoes further changes.[1] With diazonium salts derived from aniline or more basic primary

$$\left[\text{Ar–N}\equiv\text{N}\right]^{+}\ {}^{-}\text{OH} \rightleftharpoons \text{Ar–N=N–OH} \quad \text{(IX)}$$

amines, the positive charge on the azo group will be correspondingly less and the equilibrium will shift more towards (IX). When the latter reacts with aniline, the diazo group coordinates with the nitrogen atom of the primary amine; a mole of water then splits off and a relatively stable diazoamino compound is formed. Diazonium salts from amines carrying



$$\text{PhNH}_2+\text{HO–}\ddot{\text{N}}\text{=}\ddot{\text{N}}\text{–Ar} \longrightarrow \text{Ph–}\overset{+}{\text{N}}\text{H}_2\,{}^{-}\text{OH}\ (\text{:}\ddot{\text{N}}\text{=:N–Ar}) \longrightarrow \text{Ph–NH–N=N–Ar}+\text{H}_2\text{O}$$

electronegative substituents in the nucleus carry a stronger positive charge on the diazonium group and the tendency for coordination with the primary amino group of aniline is less; when the diazonium group is capable of functioning as a powerful cationoid group or a cation, it will attack a negatively polarized position in the nucleus rather than the amino group.

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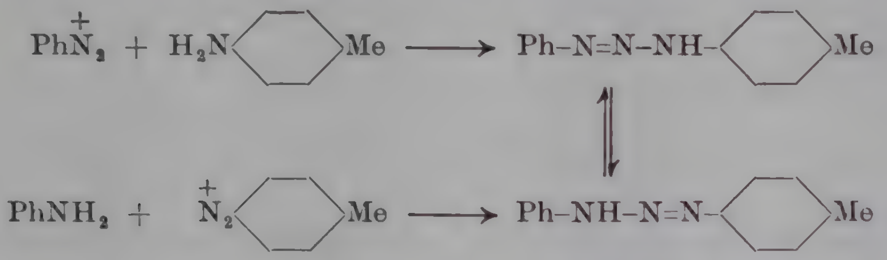
[14] *Ber.* **48**, 1398 (1915).

[15] *JCS* 1383 (**1939**); see also Philippi and Ulmer-Plenk, *Ber.* **74**, 1529 (1941); Holzach and Simon, *ibid.* **75**, 166 (1942).

[1] See p. 409.

The direct attachment of the diazonium radical to the nucleus is further facilitated when the electron density in the coupling position is increased by the presence of electron-donating groups, such as amino or methyl, in the *o*-position to the site of coupling (i.e., the *m*-position to the directing amino group). Thus *m*-phenylenediamine couples rapidly and in one stage to form the diaminoazo compound.

The system $Ar^1{-}N{=}N{-}NH{-}Ar^2$ is tautomeric with $Ar^1{-}NH{-}N{=}N{-}Ar^2$ and the predominant direction in which such a tautomerization takes place depends on the relative stability of the two forms. The same compound is obtained by condensing benzenediazonium chloride with *p*-toluidine and by condensing diazotized *p*-toluidine with aniline. The product is more likely to exist as (X) because of the greater basicity of *p*-toluidine;

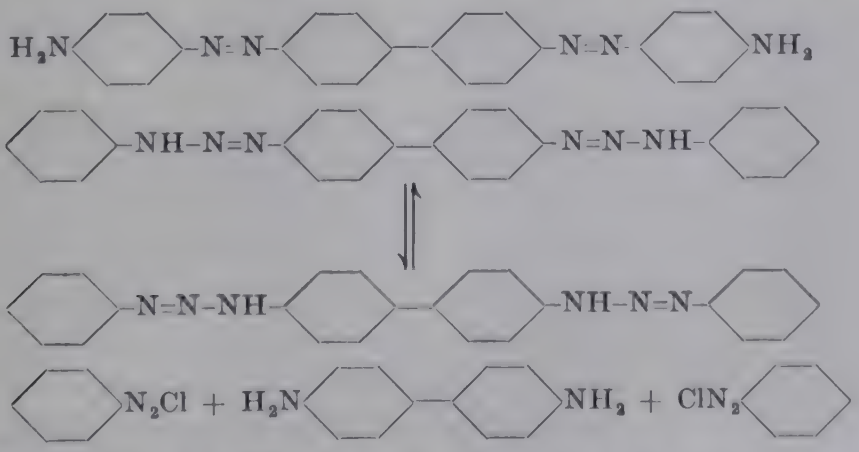


(X)

(XI)

in the triazene structures (X) and (XI) the nitrogen attached to the *p*-tolyl nucleus will attract the proton more powerfully and stabilize the structure (X). However, the structures (X) and (XI) will be in equilibrium, the proportions depending not only on their stability but also on the solvent, pH and temperature. The triazene system is analogous to the three-carbon system with the difference that the former is more polarizable.

Similar considerations of relative stability in a tautomeric system may be involved in a well-known anomaly in the behavior of aniline on treatment with tetrazotized benzidine. Neither the azo dye (XII) nor the



(XII)

(XIII)

(XIV)

diazoamino compound (XIII) is obtained; and the product is a mixture of benzidine and benzenediazonium chloride.[16] It is probable that the diazoamino compound (XIII) is first formed, and tautomerizes to the more stable bis-diazobenzidine (XIV), for the same reason as in the case cited earlier—the greater basicity of benzidine in comparison with aniline. The hydrochloric acid present in the reaction mixture finally effects the fission of (XIV) into benzidine and benzenediazonium chloride. This phenomenon of diazo exchange can be a serious cause of low yields in the manufacture of disazo and polyazo dyes.

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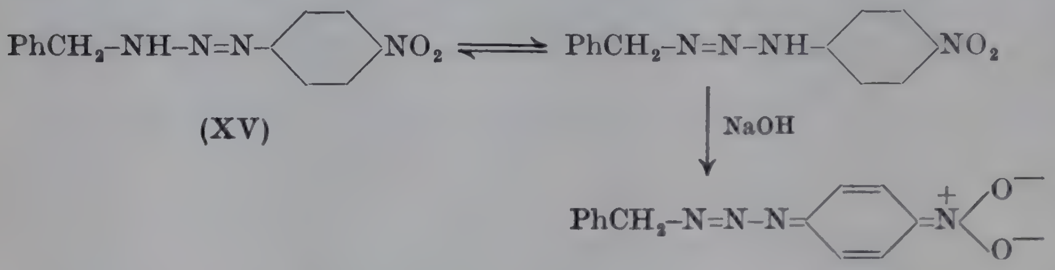
[16] For other examples of diazo exchange, see Norman, *JCS* **115**, 675 (1919).

The proton in the triazene system –N=N–NH– may move to another part of the molecule under the influence of a more powerful nucleophilic attraction. The condensation of benzylamine with *p*-nitrophenyldiazonium chloride leads to (XV), but treatment with aqueous caustic soda produces

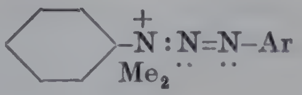


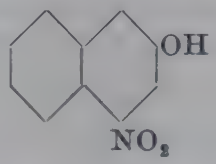
(XV) (XVI) (XVII)

a red color due to the formation of (XVII) through the intermediate benzyldiazoaminobenzene (XVI).[17]

In tertiary amines two factors favor nuclear coupling. One is the stronger anionoid character of the 4-carbon atom, in comparison with that of aniline. The other is the inability of the positively charged coordination complex (XVIII), which may possibly be formed by attachment of the diazo group

(XVIII)





(XIX)

to the nitrogen of the tertiary amine, to change into a more stable diazoamino compound.

Influence of nuclear substituents in phenols and amines. *m*-Nitroaniline, metanilic acid and *m*-chloroaniline do not couple under ordinary conditions. *N*,*N*-diethylmetanilic acid can couple with 2,4-dinitrophenyldiazonium chloride (cf. Colour Index, 50). *m*-Aminophenol couples readily, but *o*- requires special conditions.[2] 1-Nitro-3-naphthol (XIX) couples with difficulty or not at all. All these phenomena are explicable from a consideration of the effect of the substituent on the position to which the hydroxyl or amino group will direct the diazonium coupling. Groups such as nitro and sulfonic groups, which diminish the electron density at the coupling position, hinder the entry of the diazo group. Thus in

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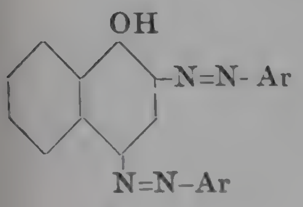
[17] Beyer, *JACS* **64**, 1318 (1942).

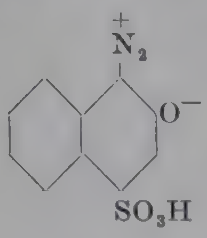
[2] See p. 409.

1-nitro-3-naphthol (XIX), the inductive and resonance effects of the nitro group decrease the electron density at the 4-position, which becomes inactivated for attack by the diazonium ion.

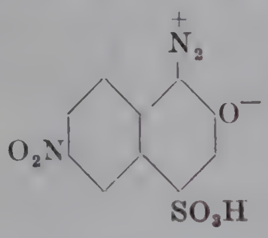
Coupling of naphthols and naphthylamines. With α-naphthol and α-naphthylamine coupling takes place mainly in the 4-position, and to a small extent in the 2-position. α-Naphthol reacts with a large excess of diazonium salt to give the 2,4-disazo compound (I). A departure from the normal coupling of α-naphthol in the 4-position of great technical importance in the preparation of mordant azo dyes is the behavior of diazotized 1-amino-2-naphthol-4-sulfonic acid (II), and its 6-nitro derivative (III); the former couples with α-naphthol largely in the 2-position, and the latter entirely,[18] leading to o,o′-dihydroxyazo dyes (IV). When the diazonium salts of 2-aminophenol-5-(or 6)-sulfonic acids, having a halogen, nitro, alkyl or acylamido substituent in the 4-position, are coupled in concentrated caustic soda solution with α-naphthol, the azo link is at the 2-position.[19] Further, if α-naphthol or α-naphthylamine carries a sulfonic group in the 3, 4 or 5-position, coupling takes place mainly or entirely in the 2-position. The relative proportions of the 4-azo compound formed with the 3- and 5-sulfonic acids depend on the diazonium salt, but further investigation seems to be necessary. 1-Naphthol-3-sulfonic acids containing a halogen or an amino group in the 5, 6, 7 or 8-position apparently couple in the 4-position, since a series of N-acylated 4-amino-1-naphthol-3-sulfonic acids have been described, for which the parent amines are prepared by reducing the azo dyes obtained by coupling diazotized p-nitroaniline with substituted 1-naphthol-3-sulfonic acids.[20]



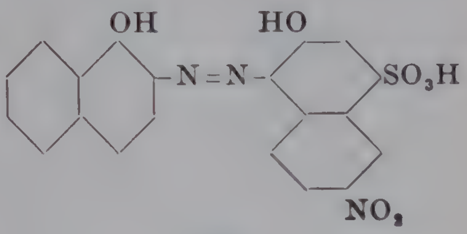
(I)



(II)



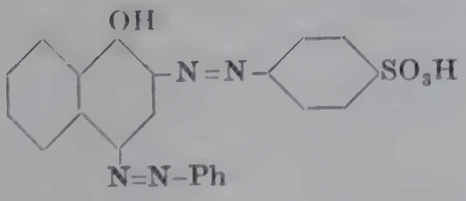
(III)

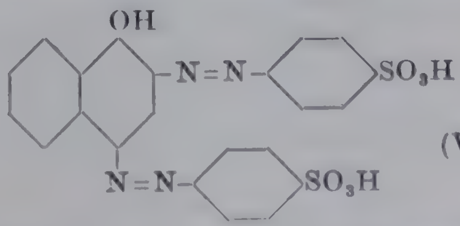


(IV)

When 4-benzeneazo-1-naphthol is coupled with diazotized sulfanilic acid, the formation of (V) would be expected; a small amount of this is

(V)





(VI)

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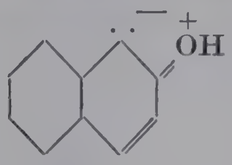
[18] Fierz-David and Brütsch, *Helv. Chim. Acta* 4, 380 (1921).

[19] Sandoz, BP 546,499.

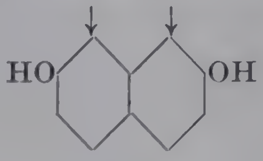
[20] Sandoz, BP 539,078.

formed, but the major product is a mixture of (I; Ar = Ph) and (VI), a curious interchange of the arylazo groups taking place.

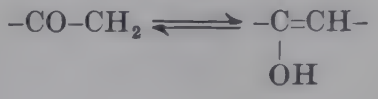
β-Naphthol and β-naphthylamine couple only in the 1-position; the structure (VII) is stabilized by the benzenoid resonance of the second ring, which is not possible when any other position is activated for attack by electrophilic substituents. This is also true of the β-naphtholate ion;



(VII)



(VIII)



$$-CO-CH_2 \rightleftharpoons -\underset{\displaystyle OH}{\underset{|}{C}}=CH-$$

(IX)

indeed the 1-position is activated more than in β-naphthol itself and the diazonium cation attacks the 1-position rapidly and exclusively. When the 1-position is occupied by an alkyl group (which by hyperconjugation opposes the resonance effect shown in (VII)), coupling does not take place; but 2,2′-dihydroxy-1,1′-dinaphthylmethane (methylene-bis-β-naphthol) couples readily to form 1-arylazo-2-naphthol. When the 1-position is occupied by a halogen, aldehyde, carboxyl or acetyl group, the substituent is replaced by the diazo group. β-Naphthol- and β-naphthylamine-8-sulfonic acids couple in the 1-position as usual, but with difficulty because of the deactivating influence of the peri-sulfonic group; this can be used for separating the 8-sulfonic acids from isomers. For the same reason R-acid couples much more rapidly than the isomeric G-acid, and the two can be thus separated.

In 2,7-dihydroxynaphthalene (VIII) coupling takes place in the 1- and 8-positions; when these are occupied by alkyl groups no coupling occurs.[21] The ability of aliphatic compounds containing a keto-enol tautomeric system (IX) to couple with diazonium salts, whereas aliphatic hydroxy compounds of the type $-CHOHCH_2-$ do not couple, shows that diazonium coupling takes place only at an enolic position. By analogy, the exclusive coupling of β-naphthol in the 1-position and of 2,7-dihydroxynaphthalene in the 1,8-positions may be interpreted as evidence of the fixation of double bonds in certain preferred positions. The tendency for such preferential fixation of double bonds in naphthalene, anthracene, etc., is also indicated by other substitution reactions and by the formation of angular, rather than linear, ring systems when derivatives of naphthalene, anthracene, etc., undergo cyclization.[22] 5-Hydroxyhydrindene (X) couples readily with a diazonium salt at the 6-position,[22] but only with difficulty at position 4. Diazonium coupling thus provides a convenient test for distinguishing between single and double bonds in a carbon-carbon linkage in which one of the carbon atoms is hydroxylated, and for locating the preferred positions of single and double bonds in aromatic ring systems.

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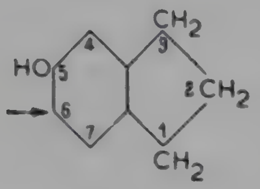
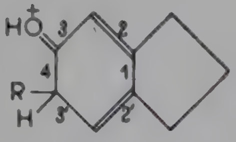
[21] Fieser and Lothrop, *JACS* **57**, 1459 (1935).

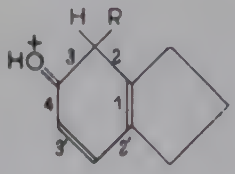
[22] Cf. Mills and Nixon, *JCS* 2510 (**1930**); for a review of the fixation of aromatic double bonds, see Rangaswami and Seshadri, *Proc. Indian Acad. Sci.* **14A,** 547 (1941).



(X)



(XA)



(XB)

These observations however should perhaps be accounted for without postulating a static system involving the fixation of bonds.[23] In the case of compounds like 5-hydroxyhydrindene and β-naphthol, where two *o*-positions are available for coupling and coupling takes place largely or exclusively in one of the two positions, alternative explanations are possible in terms of the relative stability of the activated complexes, or differences in the energy of activation, owing to the larger number of resonance structures in which the favored position is activated. The preferred positions become the only positions in which coupling takes place because of the very high reactivity of the diazonium cation. Longuet-Higgins and Coulson[24, 25] have calculated, by the method of molecular orbitals, that in hydrindene the differences in bond order and length compared to those in benzene are very small, and in the opposite direction to those commonly postulated; and they have tentatively suggested an alternative explanation of the "Mills-Nixon effect." The reaction of a cationoid reagent R^+ with 5-hydroxyhydrindene may be assumed to proceed through the intermediate transition complex (XA and XB). The steric forces in hydrindene tend to shorten bonds 1, 2 and 2′, and to lengthen bonds 3, 3′ and 4. Hence the formation of (XB) might be expected to require a greater energy of activation than (XA). No satisfactory explanation, however, seems to be available for the complete blocking of diazonium coupling by the alkyl group in 1-methyl-2-naphthol, for the displacement of chlorine, acetyl and carboxyl groups from 1-substituted-2-naphthols and for certain other anomalies in displacements of atoms and groups during diazonium coupling.

2-Naphthol-1-sulfonic acid does not couple with *p*-nitrobenzenediazonium chloride, but in acid solution the diazosulfonate (XI) can be prepared.

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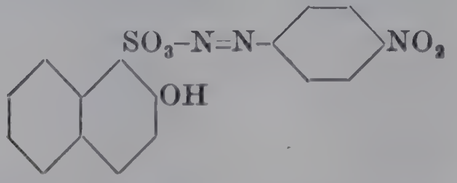
[23] Cf. Anantakrishman, *Current Sci.* (*India*) **16**, 141 (1947); Berthier and Pullman, *Bull. soc. chim. France* 88 (**1950**).

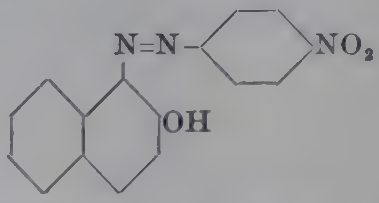
[24] *Trans. Faraday Soc.* **42,** 756 (1946).

[25] See also Pullman, *Bull. soc. chim. France* 337 (**1947**); Parkes, *JCS* 2143 (**1948**).

When this compound is dissolved in alkali and the solution is acidified, Para Red (XII) is precipitated; thus the ultimate effect is the replacement of the sulfonic group by the diazonium group.[1]

(XI)

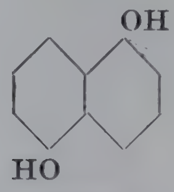




(XII)

β-Naphthol and β-naphthylamine substituted by a sulfonic group in the 8-position couple very slowly, probably due to a steric influence. Sulfonic groups in other positions do not interfere. 2-Naphthylamine-8-sulfonic acid tends to form a diazoamine, and not an azo dye, when it is treated with a diazonium salt. While β-naphthylamine substituted in the 1-position usually does not react with diazonium salts, 1-chloro-2-naphthylamine behaves abnormally on treatment with diazotized 1-nitro-2-naphthylamine; the product is the diazonium salt of 1-chloro-2-naphthylamine.[13]

1,5-Dihydroxynaphthalene (XIII) couples in the 4-position under weakly alkaline conditions, and in the 2-position under stronger alkaline conditions.[26] In the former case the compound behaves like α-naphthol



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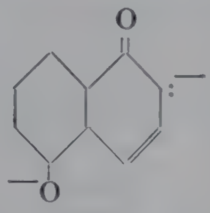
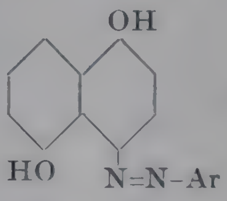
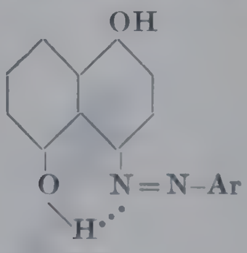


(XIV)

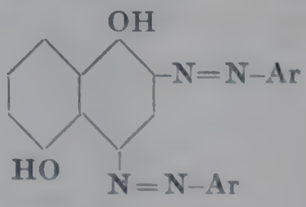


(XV)

in which the first coupling is usually in the *p*-position. With more alkali, both the hydroxyl groups ionize, and the resonance effect (XIV) activates the 2-position and not the position peri- to the ionic oxygen. With weakly polarized diazonium salts only a monoazo dye is obtained in either case;



(XVI)



(XVII)

but if the 4-monoazo dye (XV) is treated with a powerful diazonium salt, a second coupling can occur in the 2-position in the same ring containing the first azo group. Hydrogen bonding between the hydroxyl and azo groups in the peri-positions as in (XVI) inactivates the 5-hydroxyl for the coupling reaction, so that the directing influence of the 1-hydroxyl functions again, leading to the 2,4-disazo dye (XVII). 1,5-Dihydroxynaphthalene-3,7-disulfonic acid couples smoothly with two moles of the same or different diazonium salts to form disazo dyes.[27]

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[1] See p. 409.

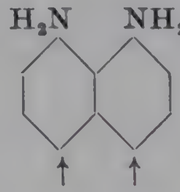
[13] See p. 417.

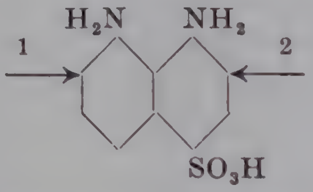
[26] Fischer and Bauer, *J. prakt. Chem.* (2), **94**, 13 (1916); **95**, 261 (1917).

1:6-Dihydroxynaphthalene couples first in the 4-position, and with a large excess of diazonium salt it is capable of forming a trisazo dye, the second and third azo groups apparently entering the 2- and 5-positions.

Diamines of the naphthalene series follow the general rules for the monamines. 1,8-Diaminonaphthalene yields the 4-monoazo and the 4,5-disazo compounds (XVIII). 1,8-Diaminonaphthalene-4-sulfonic acid couples in the 7- and 2,7-positions (XIX); because of the deactivating influence of the sulfonic group, coupling in the 7-position requires a lower activation energy and takes place first. The 4,5-disulfonic acid behaves similarly. 2,6- and 2,7-Diaminonaphthalenes couple in the 1,5- and the 1,8-positions, exactly like the dihydroxy analogs.

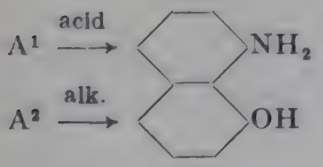
(XVIII)



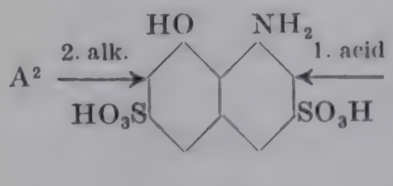


(XIX)

Coupling of aminonaphthols and their sulfonic acids. These reactions are of great importance in the preparation of a variety of azo dyes. In a coupling conducted under acidic conditions, the amino group is the directing factor; under alkaline conditions the hydroxyl group directs the coupling; and by successive couplings disazo dyes usually can be prepared. In a dual coupling, the slower acid coupling must be carried out first, followed by the much more rapid alkaline coupling. 1-Amino-8-naphthol (I) couples in the 4-position under acid conditions, and in the 5-position under alkaline conditions; and the disazo compound can be obtained by successive coupling. 1-Amino-5-naphthol, coupled with 1 mole of a diazonium salt at various pH values, gives the *o*- and *p*-hydroxyazo and *o*-aminoazo dyes. *p*-Nitrobenzenediazonium chloride at



(I)



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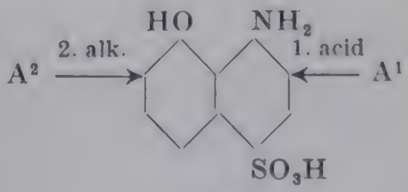

(III)

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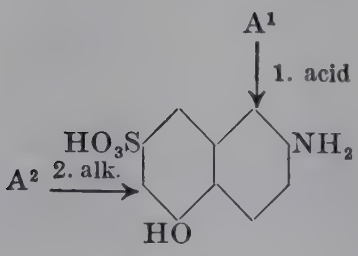
[27] Schindhelm, Schultis and General Aniline Works, USP 2,151,531.

all pH values gives almost exclusively the hydroxyazo compound; the *p*- predominates in alkaline solution and the yield of *o*- increases with decreasing pH. Benzenediazonium chloride gives the *o*-aminoazo dye at pH below 6.[28] Because of the influence of the sulfonic groups mentioned earlier, H-acid (II) and S-acid (III) couple in the 2- and 7-positions. Dual coupling is also possible in the case of J-acid (IV), and there are commercial dyes prepared in this manner. Acid coupling of J-acid is important also because the products can be converted into triazoles, which can then be alkali-coupled with diazonium salts to form useful dyes. While alkaline coupling of J-acid normally takes place *ortho* to the hydroxyl group as indicated, Wanner[29] has observed that diazotized 4-aminoazobenzene-2-sulfonic acid couples partly in the *p*-position.

In the case of γ-acid, unlike J-acid and H-acid, the disazo dye cannot be prepared; the inability of the monoazo dye (V) to undergo a second coupling under alkaline conditions like H-acid is probably due to hydrogen bonding between the 8-hydroxyl and an azo nitrogen. This suggestion finds confirmation in the behavior of M-acid (VI), which couples *para* to the amino group under acid conditions, and *ortho* to the hydroxyl under alkaline conditions; but as with γ-acid the monoazo dye (VII) will not couple again.



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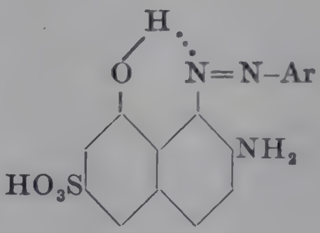

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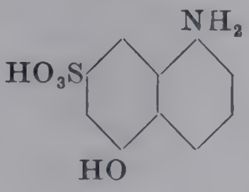

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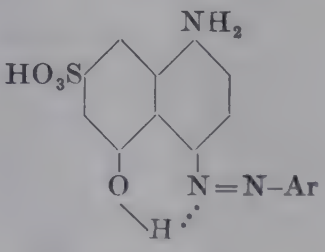

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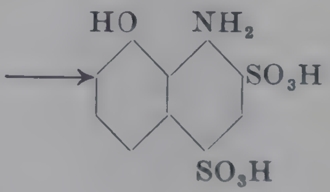

(VIII)

Chicago acid (VIII) can only couple once, in the 7-position; 1-amino-2-naphthol-4-sulfonic acid cannot couple with a diazonium salt.

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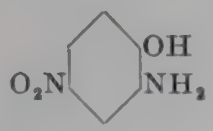
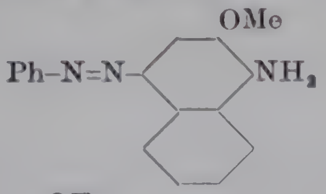
[28] Poraî-Koshits *et al.*, *J. Gen. Chem. U.S.S.R.* **15**, 446 (1945); **17**, 1758 (1947); and other papers.

[29] Dissertation Zurich, 1924, quoted in Fierz-David, Kunstliche Organische Farbstoffe, Springer, Berlin, 1926, p. 105.

Coupling in pyridine solution. β-Naphthol, which is normally coupled in alkaline solution, can also undergo coupling in dry pyridine; the attraction of a proton by pyridine produces sufficient ionisation for reaction at the 1-position. Aqueous pyridine can facilitate diazonium coupling in cases in which little or no coupling occurs in aqueous caustic soda or sodium carbonate and its role in such couplings is still obscure.[26, 30] Some slow couplings in aqueous alkali are speeded up by the addition of pyridine; and there are instances in which coupling takes place to a very small extent even after prolonged agitation of an aqueous alkaline solution of a phenol or naphthol with a diazonium salt, but where substantial yields of the azo dye are obtained if the same components interact in a pyridine medium. References to the use of pyridine for diazonium coupling are mainly in the patent literature,[31] and in the examples quoted, the sluggish character of the coupling reaction is due to the nature of the diazonium component, which is a diazotized *p*-aminoazobenzene, aminoazonaphthalene, aminodisazo dye, or an *o*-aminophenol derivative. A hydroxyl or alkoxyl group *ortho* to the diazonium group appears to be a characteristic feature of the diazonium salts which give improved yields of dyes when coupling is effected in a pyridine medium. Examples are the diazonium salts of 4-nitro-2-aminophenol (I), the monoazo dye (II), and the disazo dye (III). In a recent patent,[32] the amine (IV), in which R is an alkyl group of three or more carbon atoms, is diazotized and coupled in the presence of pyridine with suitable components, the dyes being applicable by the metachrome process. The copper complex of a disazo dye containing a free amino group has been diazotized and coupled with phenyl-J-acid in pyridine solution.[33] A pyridine-ammonia medium is used in coupling tetrazotized dianisidine with two moles of the monoazo dye (anthranilic acid $\xrightarrow{\text{acid}}$ J-acid).[34] Examples of commercial dyes prepared by the use of pyridine are Benzo Fast Copper Blue F3GL[35] and Sirius Blue 6G; the latter is the

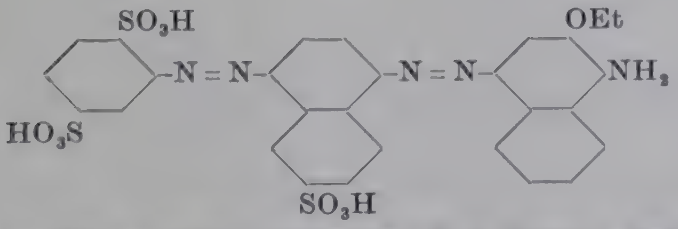
(I)

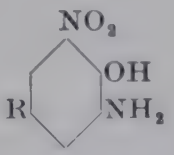




(II)

(III)





(IV)

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[26] See p. 424.

[30] Cf. Heller, *J. prakt. Chem.* (2), 77, 190 (1908).

[31] Bayer, BP 248,230; 298,518.

[32] Geigy, BP 561,228.

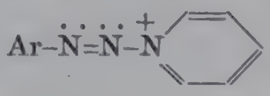
[33] Sandoz, BP 571,334.

[34] Geigy, BP 579,063; see also BP 594,325; USP 2,417,306.

[35] See Chapter XVII.

trisazo dye made by the successive diazotizing and coupling reactions (aniline-2:5-disulfonic acid ⟶ α-naphthylamine ⟶ 2-ethoxy-1-naphthylamine-6-sulfonic acid ⟶ phenyl-J-acid).[36] In the last stage practically no coupling occurs in aqueous alkali, but a 20% yield of the trisazo dye is obtained in 50% aqueous pyridine containing ammonia. A technical mixture of pyridine bases with the addition of sodium carbonate is used for coupling the disazo dye (1-amino-2-naphthol-4-sulfonic acid $\xrightarrow{\text{acid}}$ *m*-aminophenol ⟶ Cleve's acid) with phenyl-J-acid; the trisazo dye gives a bright blue copper complex which is a fast dye for cotton.[33] The end components mentioned are mainly J-acid derivatives, because of the requirements of shade and affinity for cotton, but J-acid couples normally with normal diazonium components.

No satisfactory explanation has been offered of the role of pyridine. It is not a matter of pH control, since inorganic buffers are ineffective. In one patent[37] pyridine is suggested as an "acid-binding agent" in the coupling of diazotized mononitro-*o*-aminophenols with 1-hydroxy-2-acylamido-4-alkyl benzenes. Solvent action may play a part, but it seems more likely that an interaction between pyridine and the diazonium salt is involved. The influence of a *p*-azo group and an *o*-hydroxyl or -alkoxyl group would be to decrease the positive polarization of the diazonium group, to make the diazonium salt a slow coupler, and to facilitate its decomposition. One effect of pyridine may be to stabilize the diazo group as a diazo-pyridinium radical (V),[38] which then attacks the anionoid carbon atom in the



(V)

coupling component. At the same time solvation of the hydroxyl group in the coupling component by pyridine will activate the site of coupling. The repulsion of the proton from the site of coupling in the activated complex[39] will also be facilitated by pyridine on account of its basic character. In contrast with reactions (such as the interaction of thionyl chloride and the carboxyl group)[40] in which the quantity of pyridine required is less than 0.1 mole, pyridine has to be employed in the present instance in large excess.

It has been stated that acetone can replace pyridine in some slow coupling reactions.[41]

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[36] See Chapter XV.

[33] See p. 427.

[37] Sandoz, BP 497,129.

[38] Heilbron *et al. JCS* 349 (**1940**).

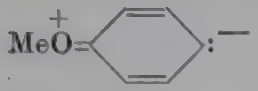
[39] See p. 411.

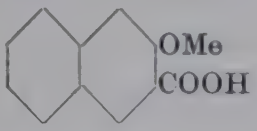
[40] Gerrard and French, *Nature* **159,** 263 (1947).

[41] Paine and ICI, BP 374,498.

Coupling of *O*-alkylphenols and *N*-acylamines. Phenol and naphthol methyl ethers couple in acetic acid solution with strongly polarized diazonium salts.[14, 42] Under these conditions the contribution made by the structure (I) in the resonance of anisole appears to be sufficient to enable

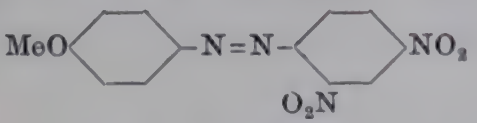
(I)





(II)

the powerful cation of 2,4-dinitrophenyldiazonium chloride to attack the 4-position. Partial or complete demethylation sometimes takes place simultaneously. The use of acetic acid is not a significant factor, and the main requirement is to bring both the reactants into solution; 2-methoxy-3-naphthoic acid (II) couples in aqueous alkaline solution, and with a series of diazonium salts coupling is accompanied by demethylation to varying degrees.[43] Available data indicate no correlation between the strength of the diazonium cation and the amount of demethylation. The coupling and demethylation reactions may take place in two ways. The aryldiazo group may first coordinate with the oxygen atom of the ether, followed by splitting off of the methyl group and migration of the aryldiazo group to a carbon atom in the *o*- or *p*-position. Alternatively, coupling on a nuclear carbon atom may take place directly, followed by demethylation. The second mechanism is more likely in the case of strongly polarized diazonium salts, since the resonance effect (I) is adequate for nuclear coupling to take place, and in the azo compound (III) the inductive and



(III)

resonance effects of the nitro groups facilitate the repulsion of the methyl group.

N-Acyl derivatives of α-naphthylamine (acetyl, benzoyl or *p*-toluenesulfonyl) have been stated to couple with diazonium salts, but less readily than the unsubstituted amine.[44] The corresponding *N*-methylamides do not couple. The azo dyes from α-acylamidonaphthalene exhibit "anhalochromism" (by analogy with "cathalochromism," usually called merely halochromism) or deepening of color on the addition of alkali; the dye from 1-benzamidonaphthalene dissolves in alcohol with an orange-yellow color, which is changed to red-violet by caustic soda.

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[14] See p. 418.

[42] König and Köhler, *Ber.* **54**, 981 (1921).

[43] Mason and Jambuserwala, *J. Soc. Dyers Colourists* **46**, 340 (1930). See also Hurd and Bonner, *JACS* **71**, 3241 (1949).

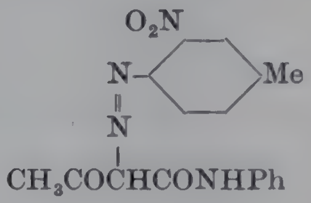
[44] Witt and Schmitt, *Ber.* **27**, 2370 (1894).

Coupling on an aliphatic or alicyclic carbon atom. Aliphatic enols couple in alkaline solution with diazonium salts. Coupling on an aliphatic carbon atom is of technical importance as a general method for the preparation of yellow dyes. 1,3-Diketones, β-ketonic acids and their derivatives can thus react. Diazonium salts couple with ethyl acetoacetate to yield the arylazoacetoacetate, which is probably in the form of the hydrazone. On treatment with acetic acid, the carboxyl group is removed and the product is the arylhydrazone of α-ketopropaldehyde ($CH_3COCH{=}N\text{-}NH\text{-}Ar$).[45]

Arylamides of β-ketonic acids are used in pigment manufacture and in azoic dyeing.[46] For the preparation of pigments acetoacetanilide (I) and its analogs are used; (II) (Hansa Yellow G) is a typical yellow pigment prepared by coupling diazotized *m*-nitro-*p*-toluidine with acetoacetanilide.

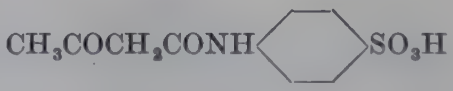
$CH_3COCH_2CONHPh$

(I)



(II)

In azoic dyeing more complex compounds are necessary to impart substantivity to the alkali enolate and adequate fastness properties to the insoluble dye produced on the fiber. As a yellow-producing component in the preparation of soluble azo dyes, the acetoacetamide derivative may contain a sulfonic group carried on an aromatic ring as in (III) or an aliphatic carbon as in (IV); these compounds can be prepared conveniently by the action of diketene with the aminosulfonic acid.[47]



(III)

$CH_3COCH_2CONHCH_2CH_2SO_3H$ (IV)

While enols couple with diazonium salts to form azo dyes in the same manner as phenols, dienols exhibit a characteristic and remarkable reaction. When a diazonium salt solution is mixed with an aqueous solution of ascorbic acid (V), a crystalline substance is formed rapidly and almost quantitatively; a series of reactions take place that lead ultimately to the arylhydrazide (VI).[48] The action of diazonium salts on ascorbic acid needs further investigation.

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[45] Chattaway and Ashworth, *JCS* 475 (**1933**).

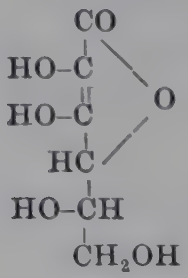
[46] See Chapter XXII.

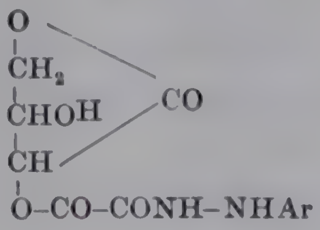
[47] MacKenzie, USP 2,328,353; 2,332,388.

[48] Weidenhagen *et al.*, *Ber.* **72**, 2010 (1939).

Carbocyclic β-diketones, like dihydroresorcinol or dimethyldihydroresorcinol (Dimedone; VII) couple with diazonium salts and such dyes are

(V)

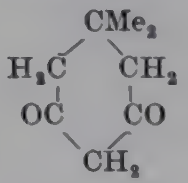


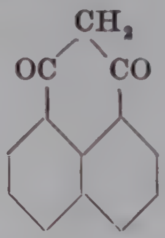


(VI)

useful for cellulose acetate.[49] The use of peri-naphthindanedione (VIII) and its derivatives as second components for the preparation of azo dyes

(VII)

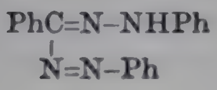




(VIII)

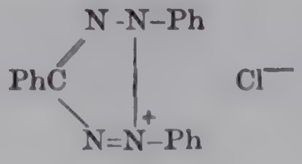
has been suggested;[50] (VIII) is prepared by heating naphthalene-1,8-dicarboxylic acid or anhydride with malonic ester at about 250°. Barbituric acid and certain of its derivatives having a reactive methylene group can undergo diazonium coupling.[51, 51a]

Diazotized aniline couples with benzaldehyde phenylhydrazone to form (IX) in 80% yield. When (IX) is treated with amyl nitrite and



$$\begin{array}{l} \mathrm{PhC{=}N{-}NHPh} \\ \;| \\ \mathrm{N{=}N{-}Ph} \end{array}$$

(IX)



(X)

alcoholic hydrochloric acid, cyclization takes place with the formation (in 67–68% yield) of triphenyltetrazolium chloride (X). The compound is colorless, but it has the interesting and useful property of imparting a red color to seeds that will germinate.[52]

Secondary nitroparaffins have been used as coupling components.[53]

A polyvinyl acetal capable of reacting with a diazo compound to form an azo dye, which will not migrate or bleed, has been suggested as a color former in photography.[54]

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[49] Eastman Kodak, USP 2,171,159.

[50] Ciba, BP 514,850.

[51] Eastman Kodak, BP 513,462.

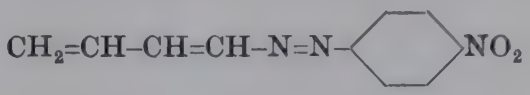
[51a] FIAT **1313**, Vol. III.

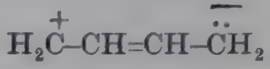
[52] *CIOS* XXVI – 73.

[53] Degering *et al.*, USP 2,441,800; 2,474,779-80.

[54] Dorough and McQueen, USP 2,380,032.

Coupling of diazonium salts with hydrocarbons. Coupling of diazotized *p*-nitroaniline with butadiene and other aliphatic dienes has been achieved by Meyer and Schoeller.[55] The reaction was carried out in acetic acid. The diazo group attaches itself to a terminal carbon atom as in (I); the butadiene therefore reacts as the polarized structure (II), with conjugative rearrangement of the double bonds after coupling. The dyes dissolve in sulfuric acid with an orange-red color, and form deeply colored complexes with mercuric chloride and stannic chloride.


(I)

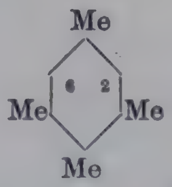

$H_2\overset{+}{C}\text{–}CH\text{=}CH\text{–}\overset{\overline{\cdot\cdot}}{C}H_2$

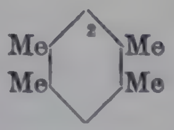
(II)

Diazotized *p*-nitroaniline and 2,4-dinitroaniline fail to couple with anthracene and mesitylene, although the solutions develop color. Meyer and Tochtermann[56] were, however, able to couple mesitylene with diazotized picramide. Smith and Paden[57] have coupled the same diazonium salt with pentamethylbenzene in a mixture of concentrated sulfuric and acetic acid. The azo compound is dark brown in the solid state, and purple when wetted with solvents. It was reduced to *C*-pentamethylaniline, which is diazotizable; the diazonium salt reacted with pentamethylbenzene in acetic acid to give a product of analysis corresponding to the formula $C_{22}H_{30}$, but which was not decamethyldiphenyl.

Diazotized picramide couples also with isodurene (III), but not with durene (IV). The difference is doubtless due to the activation of the 2- and 6-positions in isodurene (III) by the methyl groups in the 1,3,5-positions; the 2-position in durene (IV) is activated only by two methyl groups and this does not lead to adequate electron density for attack by the diazonium ion. The potent carcinogenic hydrocarbons, methylcholanthrene and 2,3-benzpyrene, couple with diazotized *p*-nitroaniline with remarkable ease.[58]

(III)





(IV)

Coupling of diazonium salts with heterocyclic compounds. Heterocyclic aromatic compounds, containing hydroxyl or amino groups, couple with diazonium salts in the usual manner. 5-Pyrazolones are the main heterocyclic compounds used as coupling components in the preparation of commercial azo dyes. They couple as 5-hydroxypyrazoles (I) and are specially valuable for the production of yellow to red dyes.[59]

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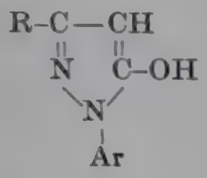
[55] *Ber.* **47,** 1711 (1914); **52,** 1468 (1919).

[56] *Ibid.* **54,** 2283 (1921).

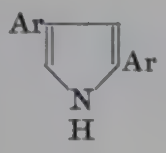
[57] *JACS* **56,** 2169 (1934).

[58] Fieser and Campbell, *ibid.* **60,** 1142 (1938).

Pyrrole couples with diazonium salts under weakly alkaline conditions and yields the α-or β-monoazo dye, corresponding to *o*- and *p*-coupling in phenol; the α-compound is the more readily formed. Under alkaline conditions and with an excess of diazonium salt, the 2, 4-disazo compound is formed. The tendency for pyrrole to couple is so marked that, as with *p*-hydroxybenzoic acid, a carboxyl group is replaced during coupling. 2,4-Diarylpyrrole (II), in which the 5-position is reactive, couples readily with diazonium salts.[60] The acid strength of pyrrole is increased considerably by the presence of the aryl groups in the 2,4-positions. In the resonance structure (IV) of the anion (III), the 5-position becomes a site of high electron density



(I)



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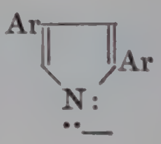

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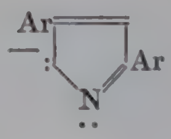
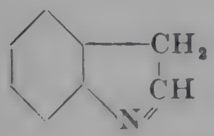
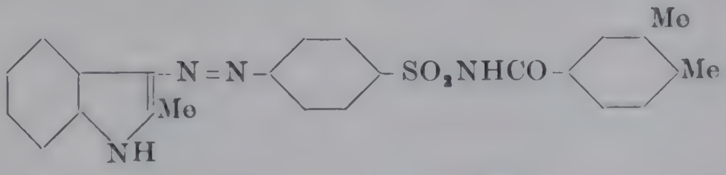


(IV)

and is readily attacked by the diazonium radical. With suitable aryl, alkyl, or acylamido substituents in the 3-position, azo dyes for wool and cotton, as well as pigments, can be prepared.[61]

Indole, when it functions as indolenine (V), contains a reactive methylene group and can react with an alkyl nitrite and sodium ethylate to give a β-isonitroso derivative. Indole also can couple with diazonium salts. It has been shown recently[62] that the diazonium salt of the sulfa drug, Irgafen

(V)




(VI)

(*N*¹-3,4-dimethylbenzoylsulfanilamide), couples with 2-methylindole, to give (VI), which has a bacteriostatic and respiration-inhibiting effect on the tubercle bacillus.

2-Hydroxycarbazole (VII), 3-hydroxydibenzofuran (VIII) and similar phenols with fused heterocyclic rings couple in the angular *o*-position in the benzene nucleus. Arylamides of the carboxylic acids of (VII) and

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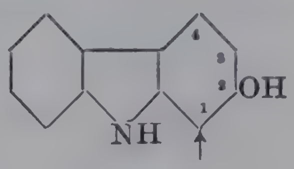
[59] See Chapter XVIII.
[60] Rogers, *JCS* 594 (**1943**).
[61] See Chapter XXXIX.
[62] Zetterberg, *Nature* **159**, 235 (1947).

(VIII) are employed as azoic coupling components.[46] 2,4- and 2,6-Diaminopyridine couple with benzenediazonium chloride to give dyes ("Pyridium") with powerful bactericidal properties. Hydroxypyridones have been mentioned as couplers for diazotype prints.[63] 2,4-Dihydroxyquinoline couples with benzenediazonium chloride to form a dye useful for cellulose acetate.[51a] Tetrahydroquinoline derivatives are also used as azo dye intermediates.[64]



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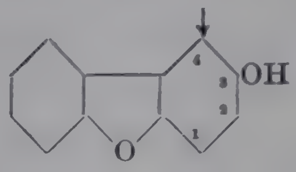
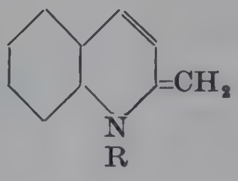
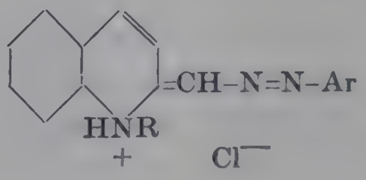


(VIII)

A solution of a quinaldinium salt treated with alkali behaves like *N*-alkyl-α (or γ)-methylenedihydroquinoline (IX) which is capable of reacting with diazonium salts on the methylene group, the dye being constituted as (X).[65]



(IX)



(X)

9-Methylacridine couples with diazonium salts to form dyes which exist as the corresponding acridine-9-aldehyde arylhydrazones or as tautomeric mixtures in which the hydrazone structure predominates. Depending on the diazonium salt used, the products behave as acid or basic dyes, which are not fast to light.[66]

4,6-Diaminopyrimidine couples with diazonium salts in the 5-position.[67]

The "sulphazone" (XI) couples with diazonium salts on the reactive methylene group, and it has been suggested as a component for the preparation of azo dyes.[67a]

2,5-Dimethylfuran reacts with *p*-nitrobenzenediazonium chloride to form an unstable product (XII) by opening of the furan ring; and on acid hydrolysis cyclization of (XII) to 1-*p*-nitrophenyl-3-acetyl-5-methylpyrazole (XIII) takes place.[68]

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[46] See p. 430.

[63] Morgan and General Aniline and Film Corp., USP 2,431,190.

[51a] See p. 431.

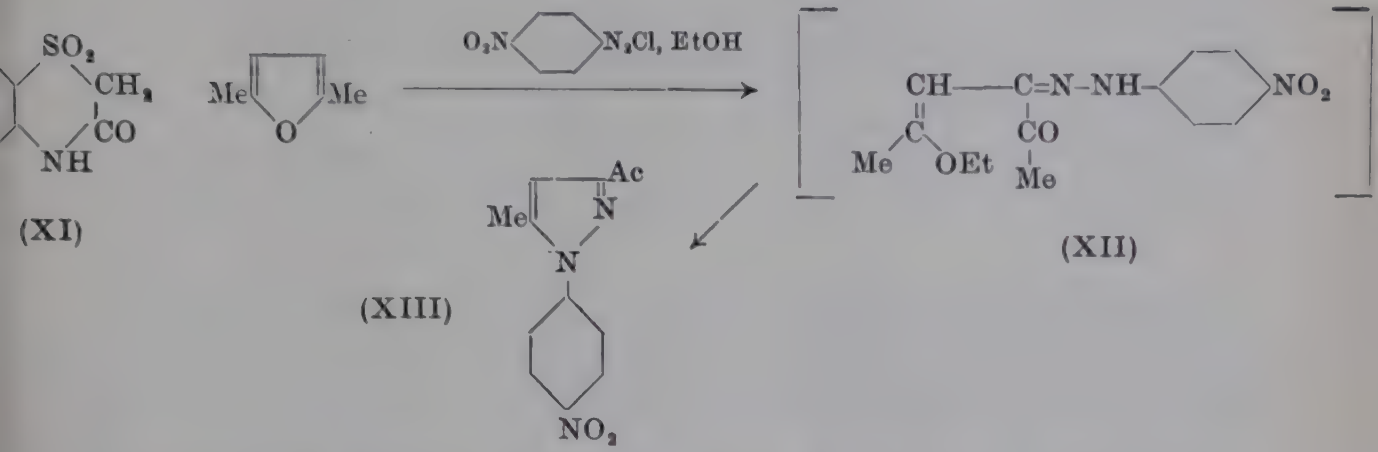
[64] See Chapter XXI.

[65] König, *Ber.* **57**, 891 (1924).

[66] Poraî-Koshits and Kharkharov, *Bull. acad. sci. U.R.S.S. Classe sci. chim.* 143 (**1944**).

[67] Lythgoe, Todd and Topham, *JCS* 315 (**1944**).

[67a] MLB, DRP 269,428; 273,342: See also Eastman Kodak, USP 2,186,629; 2,466,397.



Coupling of natural phenolic coloring matters. Many natural coloring matters of the chalkone, flavone, and pyran groups contain the resorcinol and phloroglucinol nucleus, and they are capable of coupling with diazonium salts. Perkin[69] utilized this reaction for characterizing a number of phenolic coloring matters, e.g., chrysin, apigenin, and euxanthone. The reaction has also been found useful for identifying some of the catechins, which are optical isomerides, and which form disazobenzene derivatives with characteristic melting points.

As early as 1876, Weselsky[70] prepared a benzeneazo derivative of cutch. In 1888 the preparation of azo dyes in substance from cutch, logwood, and quercitron bark was patented.[71] Recently the utility of the reaction for altering the shades and improving the fastness of cutch dyeings, and for calico printing, has been examined.[72] While a range of bright and attractive shades (golden brown to chocolate and purple) can be obtained, the dyes possess only moderate fastness to most agencies and poor fastness to chlorine. Azo dyes giving yellow to brown shades on leather are produced by coupling catechin with diazonium salts containing *o*-hydroxy or carboxy groups and converting the acid-mordant colors into metal complexes.[73] Old fustic may also be used as the coupling component.

6-Hydroxyflavone couples with diazotized aniline to form the 5-monoazo dye, formulated as (I) in view of the tendency for one of the Kekulé structures of the benzene ring in chromone to be stabilized by fusion with the γ-pyrone ring.[74] The constitution of the dye (I) was confirmed by its reduction to an amine, which on diazotization and hydrolysis gave 5,6-dihydroxyflavone (II).[75]

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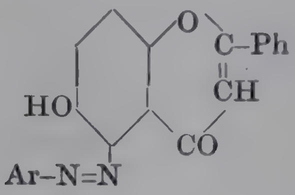
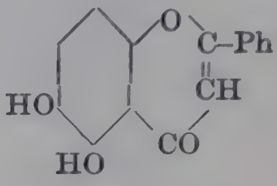
[68] Eastman and Detert, *JACS* **70**, 962 (1948).
[69] *JCS* **69**, 1439 (1896); **73**, 666 (1898).
[70] Weselsky, *Ber.* **9**, 217 (1876); see also Everest, *J. Soc. Dyers Colourists* **36**, 49 (1920).
[71] Thompson and Claus, BP 14,836.
[72] Ramachandran and Venkataraman, *J. Soc. Dyers Colourists* **54**, 513 (1938); IP 24,056.
[73] ICI, BP 418,381; 421,054.

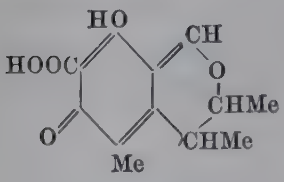


(I)

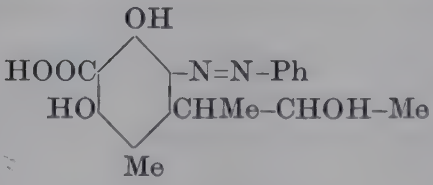


(II)

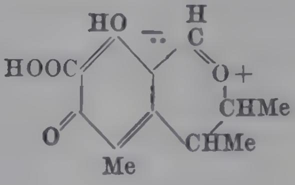
An interesting application of the diazo coupling reaction in the investigation of constitutional problems is to citrinin, the yellow phenolic coloring matter isolated by Hetherington and Raistrick[76] as a metabolic product of *Penicillium citrinum* Thom. The constitution originally assigned to it[77] has been shown to be untenable. Citrinin (III) reacts with diazonium salts in a remarkable manner, giving a mixture of products; under specific conditions the main product with diazotized aniline is (IV), and the mechanism of the reaction is apparently a direct electrophilic attack of the diazonium cation on the coupling site which has a high electron density in the resonance structure (V) for citrinin.[78]



(III)



(IV)



(V)

Coupling of oxycellulose. Oxycellulose reacts with diazonium salts to form colored products.[79] Tetrazotized benzidine was found to be more reactive, and the development of the yellowish-brown color, which did not take place in acid solution and was feeble in the presence of sodium acetate, was most marked in presence of sodium carbonate or caustic soda. A closer investigation[80] of the phenomenon showed that the ability to couple with diazonium salts is not associated with all oxycelluloses, but is restricted to certain types. A copper number of two or more is necessary for distinct reactivity, but reducing power is not the only criterion. Oxycelluloses prepared by treatment of cellulose with alkaline hypochlorite and acidic permanganate couple with diazonium salts, but oxycelluloses of equivalent copper number prepared by the action of alkaline permanganate and strongly alkaline sodium hypobromite or nitric acid exhibit no coupling power. Cellulose modified by the action of sunlight or ultraviolet light is also unaffected by diazonium salts. It has been suggested that the oxycelluloses possessing diazo coupling power are characterized by a β-ketonic acid or aldehyde group.[81]

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[74] Mahal and Venkataraman, *Current Sci.* (*India*), **6,** 450 (1938).

[75] Iyer and Venkataraman, *Proc. Indian Acad. Sci.* **23A,** 278 (1946).

[76] *Trans. Roy. Soc. London* **220,** 269 (1931).

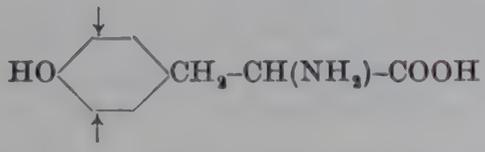
[77] Coyne, Raistrick and Robinson, *ibid.* **220,** 297 (1931).

[78] Gore, Panse and Venkataraman, *Proc. Indian Acad. Sci.* **29A,** 289 (1949). See also Cartwright *et al., JCS* 867; 1563 (**1949**).

[79] Everest and Hall, *J. Soc. Dyers Colourists* **37,** 229 (1921); **39,** 47 (1923).

[80] Forster, Kaji and Venkataraman, *J. Indian Chem. Soc. Ind. News Ed.* **1,** 36 (1938).

Coupling of wool and silk. Diazonium salts couple with proteins by virtue of the phenolic group in the tyrosine units and the indole group in the tryptophane units. Both keratin of wool and fibroin of silk have tyrosine as a constituent; in fibroin tyrosine constitutes about 13% of the total amino acids. When silk is treated with diazonium salts[82] in presence of sodium acetate, yellow, orange, brown and maroon shades are obtainable. The shades are similar to those of azo dyes derived from simple phenolic coupling components, but the size of the protein molecule leads to greatly increased fastness to light and washing.[83] In alkaline solution, tyrosine (I) couples at either one or both positions ortho to the phenolic hydroxyl. The dye produced on the silk fiber, however, is of a complex character. The fiber absorbs some of the diazonium salt, particularly if it is in excess of two moles per one tyrosine unit in the protein; on soaping, the uncoupled diazonium salt hydrolyses partly to the corresponding phenol, which then couples with the undecomposed diazonium salt.



(I)

Acid and basic dyes containing a free amino group may be dyed on silk, then diazotized and coupled with the fiber; relatively loose shades thus become faster.

By treatment of union fabrics of silk and cellulose fiber with diazonium salts, colored and white effects can be produced since the cellulose is unaffected. The action of diazonium salts on silk can also be utilized for identifying and estimating the fiber in admixture with fibers which do not undergo this reaction.[83]

Waste leather may be used for the production of dyestuffs by coupling with diazonium salts or by oxidation in presence of amines.[84]

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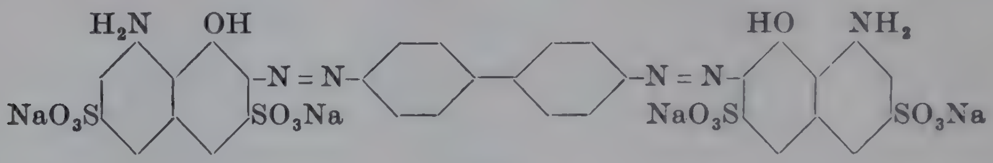
[81] Kaji and Venkataraman, *Current Sci.* (*India*) **9,** 66 (1940).

[82] Sisley *et al.*, *Bull. soc. chim. France* **41,** 1217 (1927); **47,** 1389 (1930).

[83] Ramachandran, Ph.D. Thesis, Bombay University, 1943.

[84] Colin-Russ, *Chem. Trade J.* **115,** 543 (1944).

Replacement reactions in diazonium coupling. Limpricht[85, 86] observed that when *p*-hydroxybenzoic acid was treated with diazotized aniline the carboxyl group was displaced with the formation of *p*-hydroxyazobenzene. The replacements of halogen,[87] sulfonic groups (via the diazosulfonate), acetyl and carboxyl groups[88] from the 1-position in β-naphthol were later noticed. When successive couplings are carried out with different diazonium salts, there is a possibility of a more strongly polarized diazonium ion displacing the arylazo group already present. Such reactions have not been extensively investigated; but Filippuichev and Chekalin found that the *p*-nitrobenzeneazo group displaced the *p*-sulfobenzeneazo group in one instance. When benzeneazo-H-acid in sodium carbonate solution was treated with tetrazotized benzidine, the disazo dye (I) was produced, together with benzeneazophenol. These displacements took place only with azonaphthols, and not with azophenols.[89]



(I)

When a triphenylmethane dye is treated with diazotized *p*-nitroaniline, one of the phenylmethane groups is split off in many cases. An examination of the azo dye is useful for identifying the triphenylmethane color.[90] Phenolphthalein is split by diazonium salts into azophenols and *o*-(*p*′-hydroxybenzoyl)benzoic acid.[90a]

By the interaction of rottlerin (the phenolic coloring matter of Kamala, the orange-red powder obtained from the fruits of *Mallotus phillipinensis*) with diazoaminobenzene, Brockmann and Maier[91] found that a methylenebisphloroglucinol underwent fission with the formation of a benzeneazophloroglucinol derivative. The fission of a ring system in citrinin has been mentioned.

The product of coupling 3-methylacetylacetone with a diazonium salt is a derivative of methyl ethyl ketone.[92] Malonic acid undergoes partial

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[85] *Ann.* **263,** 237 (1891).

[86] See also Grandmougin and Freimann, *Ber.* **40,** 3453 (1907); *J. prakt. Chem.* (2), **78,** 401 (1908); Kostanecki and Zibell, *Ber.* **24,** 1696 (1891).

[87] Hewitt and Mitchell, *JCS* **89,** 1167 (1906).

[88] Fries and Schimmelschmidt, *Ber.* **58,** 2835 (1925).

[89] Filippuichev and Chekalin, *Anilinokrasochnaya Prom.* **5,** 76 (1935).

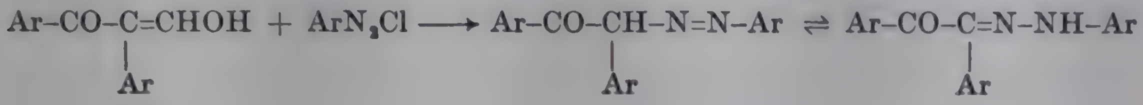
[90] Green, *J. Soc. Dyers Colourists* **45,** 141 (1929).

[90a] Ziegler and Zigeuner, *Sitzungsber. Öster. Akad. Wiss.* **158,** (2), 313 1949; contrast Leandri, *Gazz. chim. ital.* **78,** 20 (1948).

[91] Brockmann and Maier, *Ann.* **535,** 175 (1938).

[92] Morgan and Reilly, *JCS* **103,** 810 (1913).

decarboxylation by diazo coupling.[93] The aldehyde group in hydroxymethylene compounds of the type of (II) is replaced by the action of diazonium salts.[94]

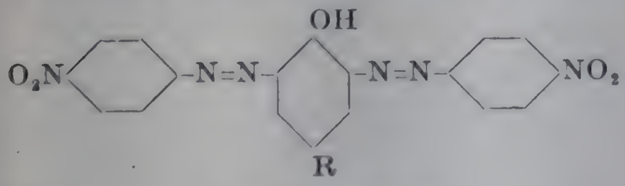


$$\underset{\substack{|\\ \text{Ar}}}{\text{Ar–CO–C}}\text{=CHOH} + \text{ArN}_2\text{Cl} \longrightarrow \underset{\substack{|\\ \text{Ar}}}{\text{Ar–CO–CH}}\text{–N=N–Ar} \rightleftharpoons \underset{\substack{|\\ \text{Ar}}}{\text{Ar–CO–C}}\text{=N–NH–Ar}$$

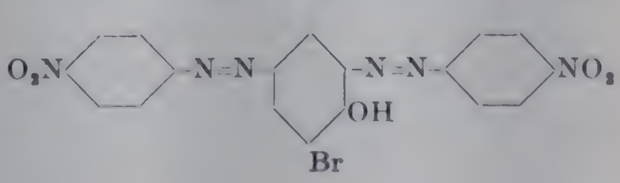
(II)

Gore and Modak[95] have confirmed and extended the earlier observations on these replacements in benzene and naphthalene derivatives. The anionoid reactivity of the 1-position in β-naphthol is so marked that the anilide of 2-hydroxy-1-naphthoic acid couples with diazonium salts, and atoms and groups such as chlorine, bromine, carboxyl, aldehyde, and acetyl are replaced by interaction even with weakly polarized diazonium salts. The replacements take place under the usual alkaline conditions of phenolic coupling, and the carboxyl group is replaced in a particularly facile manner, since a neutral carbon dioxide molecule can be easily split off from the $-CO_2$ ion, leaving behind an electronegative site to which the diazonium cation can be attached. The chlorine atom is removed as a chloride ion by the resonance of the naphtholate ion in which the 1-position becomes a site of high electron density. The groups which are not replaced by diazonium coupling are alkyl (but not alkylene, which can be replaced), amino and nitro groups; the stability in the last case is due to the strong chelation in 1-nitro-2-naphthol. Alkyl and amino groups, on account of their electron-donor character, oppose the resonance of the naphtholate ion.

In the benzene series, a carboxyl group *para* to a hydroxyl, as in *p*-hydroxybenzoic acid or β-resorcylic acid, is readily displaced, but the carboxyl group in salicylic acid and in 3- and 5-substituted salicylic acids can only be replaced by a strongly polarized diazonium radical. When 5-chloro, 5-acetyl or 5-methyl salicylic acid is treated with a large excess of diazotized *p*-nitroaniline or 2,5-dichloroaniline, the carboxyl group is partially replaced with the formation of the disazo dyes (III), but the chlorine atom, the acetyl group and the alkyl group are intact. 4-Aminosalicylic acid couples with benzenediazonium chloride partly by replacement



(III) R=Cl, Ac or Me



(IV)

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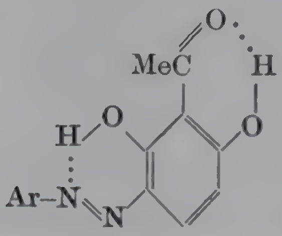
[93] v. Pechmann, *Ber.* **25**, 3175 (1892); Busch and Wolbring, *J. prakt. Chem.* (2), **71**, 370 (1905).

[94] Roy and Sen, *J. Indian Chem. Soc.* **10**, 347 (1933).

[95] Unpublished work.

of the carboxyl group, although the position *para* to the hydroxyl group is free. If 3,5-dibromosalicylic acid is coupled with diazotized *p*-nitroaniline, the product is (IV), the carboxyl group and the bromine atom *para* to the hydroxyl being displaced. Similar results are obtained in the case of resorcinol.[96]

The reaction of resacetophenone, 2,6-dihydroxyacetophenone, or 4,6-diacetoresorcinol with a large excess of diazotized *p*-nitroaniline results in no displacement of the acetyl groups, and coupling takes place only in the vacant *o*- and *p*-positions. While resacetophenone readily forms the 3,5-disazo compound, 2,6-dihydroxyacetophenone undergoes the first coupling less readily than resacetophenone, requiring a higher pH, and the second coupling does not go to completion even with three moles of the diazonium salt. When the monoazo compound has been formed, the chelations shown in (V) deactivate the available coupling position. While β-resorcylic acid gives a mixture of 4-benzeneazoresorcinol and 5-benzeneazo-β-resorcylic acid even with one mole of benzenediazonium chloride, γ-resorcylic acid undergoes no decarboxylation with one mole of the diazonium salt, and with two moles 4,6-bisbenzeneazoresorcinol-2-carboxylic acid is formed in good yield.



(V)

The diazo coupling reaction in quantitative analysis. The quantitative character of the diazo coupling reaction makes it useful for the estimation of diazotizable amines and of amines and phenols which have a free coupling position. There is no organic reaction of wider applicability for quantitative estimations. In addition to the estimation of amines and phenols which are intermediates in the dyestuff industry, the method has been used for a large variety of synthetic and natural compounds. Since the product of the diazo coupling reaction is in all cases colored, and since the color of the product and its solubility in water can be varied at will by using suitable coupling components, the method is of special value for the colorimetric estimation of substances occurring in minute quantities. Thus γ-tocopherol (I) can be determined colorimetrically in presence of α- and β-tocopherols by taking advantage of its ability to couple with a diazonium salt;[97] the inability of β-tocopherol (II) to couple is an indication of the tendency for bond fixation as with 1-methyl-2-naphthol. Thiamin is estimated as the azo dye formed by coupling it with diazotized

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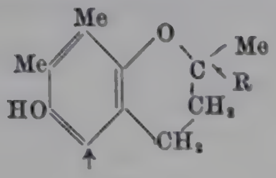
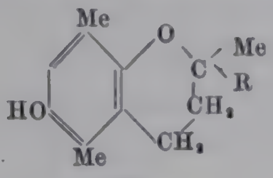
[96] Cf. debrominations of bromophenols; e.g. Kohn and Reichmann, *J. Org. Chem.* **12**, 213 (1947).

[97] Quaife, *JACS* **66**, 308 (1944).


(I)


(II)

p-aminoacetophenone. The sulfanilamides can all be estimated by diazotizing the free amino group and coupling the diazonium salt with a suitable phenol or amine (e.g., *N*-1-naphthyl ethylenediamine).[98]

Preparation of azo dyes by methods other than diazonium coupling. Azo dyes can be prepared by (*a*) the alkaline reduction of aromatic nitro compounds (cf. the preparation of azobenzene); (*b*) the condensation of aromatic nitro or nitroso compounds with arylamines; and (*c*) the oxidation of primary aromatic amines. Such special methods are used for the preparation of some azo dyes of the thiazole and stilbene series, and examples are cited in Chapters XIX and XX.[98a]

CONSTITUTION OF AZO DYES

***Cis-trans* configuration.** Azobenzene normally has the *trans*-configuration,[99] which appears to be the stable orientation of the C-N=N-C group. The *trans*-configuration of all stable azo compounds is supported by dipole moment evidence.[100] Ordinary (*trans*-) azobenzene is partly converted into the *cis*-form on exposure of the solutions to light.[101] The darkening of solutions of several derivatives of azobenzene on exposure to light is due to partial conversion into the *cis*-forms.

Cook[102] has shown that a solution of irradiated azobenzene can be easily separated into *cis*- and *trans*-isomerides by the preferential adsorption of the former on active alumina, and the generality of such isomerism was indicated by the preparation of several substituted azobenzenes in *cis*-modifications. The absorption spectra of numerous substituted *cis*-azobenzenes, determined in chloroform solution from 2800 to 4800A., exhibit the two-banded structure of the spectra of the *trans*-isomerides; the intensity of the absorption rather than the trivial changes in wave length provides the chief distinguishing features.[103, 104] Cook and Jones[103] have ascribed a *trans-trans* configuration to *p*-bisbenzeneazobenzene, but they have obtained evidence of the ability of the azo linkages to undergo independent

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[98] Bratton *et al.*, *J. Biol. Chem.* **128,** 537 (1939).

[98a] See also Martynoff, *Compt. rend.* **223,** 747 (1946); **225,** 1332 (1947); **227,** 1371 (1948); Geigy, SP 241,207; Badger *et al.*, *Proc. Roy. Soc. London* **B130,** 255 (1941); Friedman, Gofstein, and Seligman, *JACS* **71,** 3010 (1949).

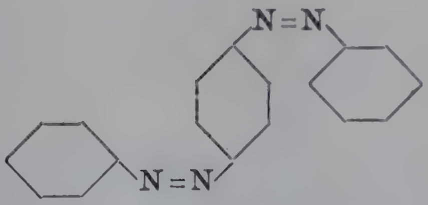
[99] Robertson *et al.*, *Proc. Roy. Soc. London* **A154,** 187 (1936).

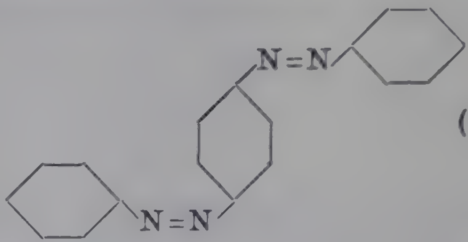
[100] Bergmann, Engel and Sándor, *Ber.* **63,** 2572 (1930).

[101] Hartley, *Nature* **140,** 281 (1937); *JCS* 633 (**1938**).

[102] *JCS* 876 (**1938**); see also Zechmeister and coworkers, *Naturwissenschaften* **26,** 495 (1938).

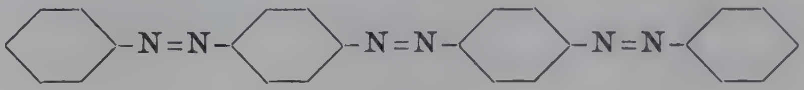
(I)





(II)

isomerization; an irradiated solution of bisbenzeneazobenzene afforded three adsorption zones clearly separated on a chromatogram, the intermediate band corresponding to the *cis-cis-* (I) and the topmost band to the *cis-trans-* compound (II). For 4,4′-bis(benzeneazo)azobenzene (III) six forms are theoretically possible, and irradiation gave indication of the formation of at least two isomerides.[105]

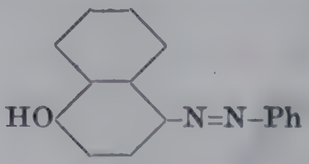


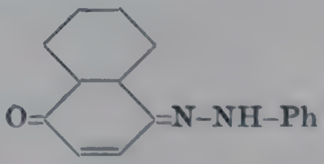
(III)

Two stages may be observed in the reduction of solutions of some azo dyes at a dropping mercury cathode, showing the presence of *cis-* and *trans-* forms. The conversion of the *trans-* to the *cis-*form by the action of light may be followed polarographically.[106]

Azophenol-quinonehydrazone tautomerism. Zincke showed in 1884 that the product of the action of phenylhydrazine on α-naphthoquinone is identical with 4-benzeneazo-1-naphthol prepared by coupling α-naphthol with diazotized aniline. 4-Benzeneazo-1-naphthol has now been shown to contain the tautomeric forms (I) and (II), which are present in sufficient quantity to give rise to characteristic absorption bands. The equilibrium

(I)





(II)

between the two forms is dependent on the solvent. Under aqueous conditions and in pyridine solution, the predominant tautomer is the azo form (I), which is stabilized by hydrogen bonding of the hydroxyl with water or pyridine. Benzene solutions contain equilibrium mixtures of the azo and hydrazone forms. In a polar solvent like nitrobenzene the quinonoid hydrazone form predominates.[107, 110]

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[103] Cook, Jones and Polya, *JCS* 1315 (**1939**).

[104] See also Fodor and Szarvas, *Ber.* **76,** 334 (1943).

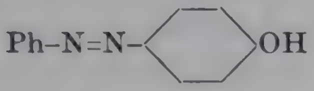
[105] For the preparation of polykisazobenzenes, free from amino and hydroxyl groups, by the condensation of nitroso compounds and primary amines, see Ruggli and Iselin, *Helv. Chim. Acta* **30,** 733 (1947).

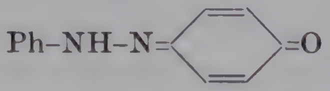
[106] Winkel and Siebert, *Ber.* **74,** 670 (1941); see also Volpi, *Gazz. chim. ital.* **77,** 473 (1947).

N-Methyl-*p*-hydroxyazo dyes obtained by condensing *N*-methylphenylhydrazine-*p*-sulfonic acid with α-naphthoquinone and its 2-methyl derivative resemble the corresponding *O*-methyl ethers and the non-alkylated dyes both chemically and in their dyeing properties.[108]

The physical and chemical properties of *p*-hydroxyazobenzene indicate that it exists in the azophenol form (III) rather than the quinonehydrazone

(III)

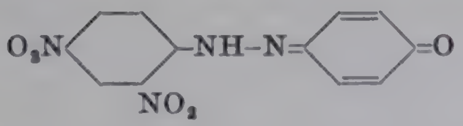




(IV)

form (IV). The absorption spectrum of the acyl derivatives of *p*-hydroxyazobenzene closely resembles the spectrum of azobenzene.[109] The azo structure for *p*-hydroxyazobenzene is supported by the dipole moment which, in benzene solution, is the same as that of phenol, the moment being exclusively determined by the hydroxyl group. It must be noted however that the dipole moment for 1-benzeneazo-2-naphthol is also that of the hydroxyl group, while the spectroscopic evidence undoubtedly favors the quinonehydrazone structure.

Evidence of the quinonoid character of certain *p*-hydroxyazo compounds, such as (V), is provided by their ability to undergo the Diels-Alder reaction; addition compounds have been obtained with cyclopentadiene. The extent of addition is influenced by the acidity of the medium and its occurrence



(V)

is not a general property of the *p*-hydroxyazo compounds.[107, 110] Further, it is obvious that the strongly electronegative nitro groups in the benzene ring not carrying the hydroxyl group would tend to stabilize the hydrazone form.

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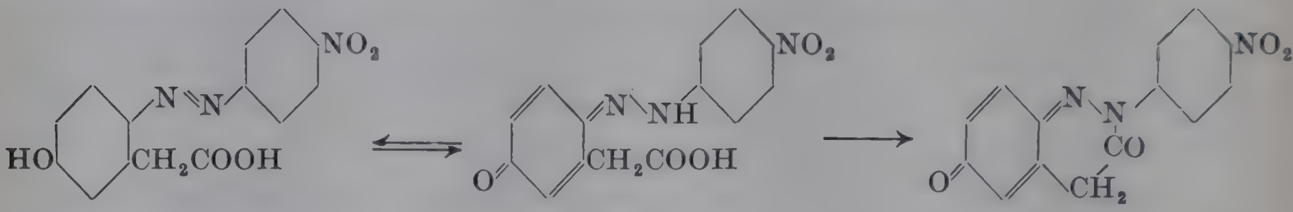
[107] Lauer and Miller, *JACS* **57,** 520 (1935); Kuhn and Bär, *Ann.* **516,** 143 (1935); Burawoy, *Ber.* **63,** 3155 (1930); **64,** 462 (1931); **66,** 228 (1933); Shingu, *Sci. Papers Inst. Phys. Chem. Research, Tokyo* **35,** 78 (1938).

[108] Fierz-David, Blangey and Streiff, *Helv. Chim. Acta* **29,** 1718 (1946). See also Ramart-Lucas *et al., Bull. soc. chim. France* 415 (**1947**).

[109] Ramart-Lucas *et al., Compt. rend.* **215,** 468 (1942); *Bull. soc. chim. France* **10,** 36, 127, 223 (1943).

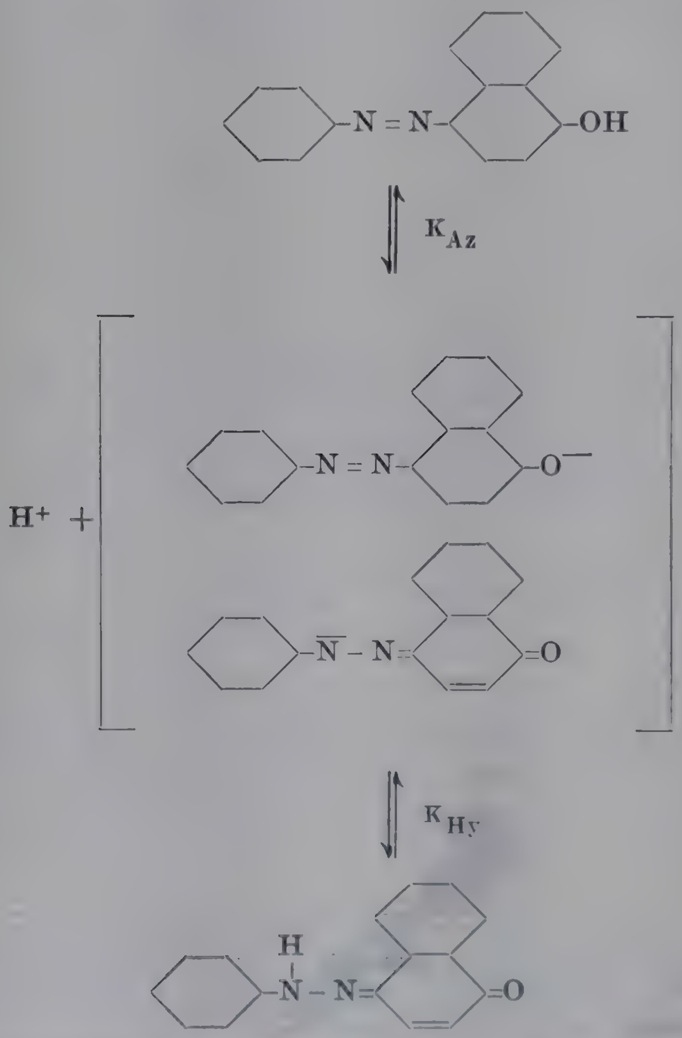
[110] Cf. Borsche, Müller and Bodenstein, *Ann.* **472,** 201 (1929); Willstätter *et al., Ann.* **477,** 161 (1929).

Benzeneazophenols (e.g., VI) react in the hydrazone form (VI A) when they undergo cyclization to the cinnoline (VII) in good yield by the action of acetic anhydride and a trace of sulfuric acid.[111]


(VI) (VIA) (VII)

Branch and Calvin [112] have discussed the azophenol-quinonehydrazone tautomerism of *p*-benzeneazophenol (A), 4-benzeneazo-1-naphthol (B) and 10-benzeneazo-9-anthrol (C) with reference to the homopolar resonance structures of the two forms. On the consideration that the change occurs only in the aromatic nucleus which undergoes the phenolic-quinoidal structure tautomerism, the ratio of the number of equivalent resonance

CHART 1



Azo

Two resonance structures of the identical ion obtained from both tautomeric forms

Hydrazone

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[111] Kornfeld, *JACS* **70**, 1373 (1948).

[112] The Theory of Organic Chemistry, Prentice-Hall, New York, 1941, p. 299.

structures in the azo form to the number in the hydrazone form is 2 for (A), 1.5 for (B) and 1 for (C). In actual fact, (A) is essentially in the azophenol form, (B) is an equilibrium mixture of the two forms, and (C) is entirely in the hydrazone form. Branch and Calvin have also examined the effect of substituents in the benzene ring on the position of the equilibrium in the case of (B), and have shown that, in accordance with their anticipation from a consideration of the equilibria in Chart I, acid-strengthening groups increase the stability of the hydrazone over the azo form. A plot of log ([Hy]/[Az]) against the constant characteristic of the substitution (calculated from the change in acid strength by substitution of phenol or the anilinium ion) is a straight line.

Chelation in *o*-hydroxyazo compounds. *o*-Hydroxyazobenzene, unlike the *p*-isomer, is volatile in steam, and it is not so readily soluble in alkali as the *p*-compound. This moderation in the hydroxylic properties of the *o*-compound as distinct from the *p*-compound is to be attributed to the chelate or hydrogen-bonded structure (I). Another indication of chelation in *o*-hydroxyazo compounds is their lower melting point in comparison with the *p*-isomers. Thus the 1-alkyl ethers of 4-benzeneazoresorcinol melt lower than the corresponding 3-alkyl ethers. *o*-Hydroxyazo compounds do not combine with dry ammonia in a non-polar solvent such as benzene or carbon tetrachloride, whereas salt formation occurs readily in a polar solvent.

As long ago as 1900, Bamberger[113] found that, in contrast to *p*-hydroxyazobenzene, the *o*-compound forms an alcohol-soluble copper salt melting at 225°. Copper, nickel, and cobalt salts of *o*-hydroxyazobenzenes and benzeneazonaphthols (1:2 or 2:1) are readily prepared by adding aqueous alcoholic copper acetate to a hot, saturated solution of the azophenol. The salts show the typical properties of coordination compounds: they are insoluble in water, sparingly soluble in polar solvents and readily soluble in non-polar solvents; and they melt to form deeply colored liquids.[114] The capacity of *o,o′*-dihydroxyazo compounds to form stable metallic complexes is of great technical importance.[115]

The *zwitterion* structure (II) proposed by Kuhn[116] for *o*-hydroxyazobenzene has not been supported by dipole moment measurements.[117] The values for *o*-hydroxyazo dyes are not abnormally high. *p*-Aminoazobenzene however has an anomalously high moment, explicable by the structure (III), which also accounts for the color change of many aminoazo dyes by the addition of acid.

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[113] *Ber.* **33,** 1951 (1900).

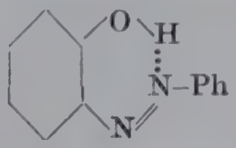
[114] Hunter *et al.*, *JCS* 1598 (**1935**); 1346 (**1938**); 653 (**1940**); 823 (**1941**); see also Haendler *et al.*, *JACS* **60,** 2813 (1938); **62,** 1669 (1940).

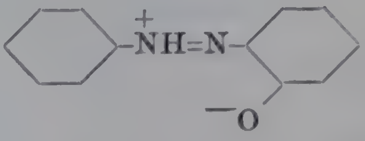
[115] See Chapters XIII and XIV.

[116] *Naturwissenschaften* **20,** 619 (1932).

[117] Bergmann and Weizmann, *Trans. Faraday Soc.* **32,** 1318 (1936).

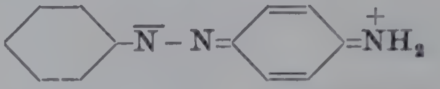
(I)





(II)

By studying the absorption spectra of the azo and hydrazone forms of azonaphthols, Ufimtsev[118] found that the difference in structure of *p*- and *o*-azonaphthols is indicated by the shift in the absorption maxima which



(III)

occurs on salt formation and ionization. With the *o*-compounds the shift is towards the shorter wave lengths, in accordance with a chelate structure. The absorption spectra of 1-benzeneazo-2-naphthol and 2-benzeneazo-1-naphthol are practically independent of the solvent and they are believed to represent the hydrazone form. From an examination of the absorption spectra of the phenylazo derivatives of β-naphthol, 6-chrysenol, 10-phenanthrol and 10-retenol, in comparison with those of their copper complexes, Haendler and Smith[119] concluded that the compounds are *o*-hydroxyazo, rather than the quinonehydrazone types. In the absorption curves of 2-benzeneazo-1-naphthol and of 2,4-bisbenzeneazo-1-naphthol, the extinction coefficient of the low frequency maximum of the disazo dye is not appreciably larger than that of either the 2- or the 4-monoazo compound, indicating that the low frequency band of these compounds is caused by one azo group existing in a state in which the other cannot simultaneously exist. One of the azo groups must therefore be assumed to be in the hydrazone form.[120, 142] From the absorption spectra, Blumberger[121] has obtained evidence of chelation between hydroxyl and azo groups in peri positions in naphthalene.

1-Benzeneazo-2-naphthol is practically insoluble in caustic soda solution; mixtures of α and β-naphthol can be thus estimated since 4-benzeneazo-1-naphthol is alkali-soluble, and the practical value of β-naphthol and its 3-carboxylic acid derivatives in dyeing is due to their forming insoluble azo dyes in the absence of sulfonic or other solubilizing groups.[46]

From the foregoing discussion it is clear that the azophenols and azonaphthols can exist in tautomeric forms; the relative stability of the tautomers varies from case to case. *o*-Hydroxyazo compounds can not only exhibit azophenol-quinonehydrazone tautomerism, but either tautomer can also exist in chelate structures, which play an important part in the fastness properties of such dyes, in mordant dyeing, and in the preparation of metal complexes in substance.

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[118] *Compt. rend. acad. sci. U.R.S.S.* **39**, 351 (1943).

[119] *JACS* **63**, 1371 (1941); **62**, 1669 (1940).

[120] Kuhn and Bär, *Ann.* **516**, 143 (1935).

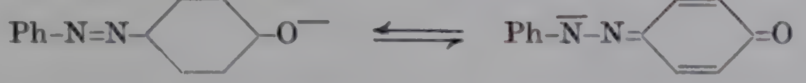
[142] Brode and Herdle, *J. Org. Chem.* **6**, 713 (1941).

[121] *Chem. Weekblad* **25**, 282, 315 (1928), *et sequa.*

[46] See p. 430.

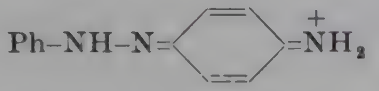
Color changes of azo dyes.[121a] *p*-Hydroxyazobenzene is soluble in aqueous alkali and the color of an alcoholic solution changes from yellow to red on the addition of aqueous caustic soda; the deepening in color is associated with the resonance structures (I) and (II) of the azophenolate ion. For this reason *p*-hydroxyazo dyes in general are sensitive to alkali. *p*-Aminoazo dyes are sensitive to acid, some to an extent which enables them to be used as indicators. The color deepening and intensification on the addition of acid are due to the cation resonating between the structures (III) and (IV).

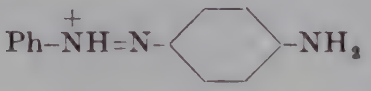
(I)



(II)

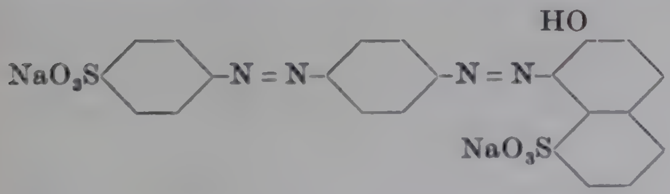
(III)



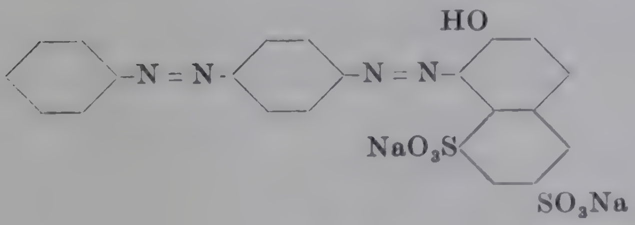


(IV)

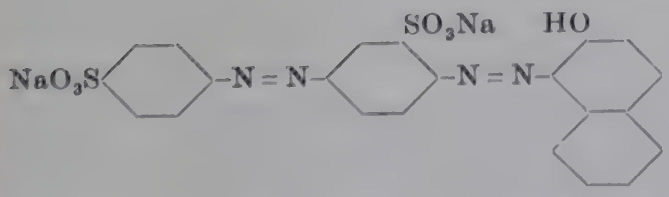
Many azo dyes exhibit in sulfuric acid solution characteristic colors, which are distinct from the colors of the solids and the aqueous solutions; they are therefore useful in identification. A striking example is the difference in the sulfuric acid colors of the three isomerides:



Blue; Crocein Scarlet 3B



Violet; Brilliant Crocein

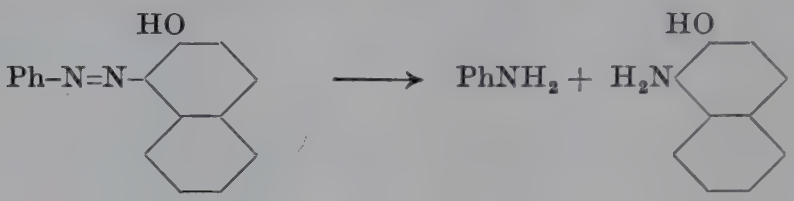


Green ; Biebrich Scarlet

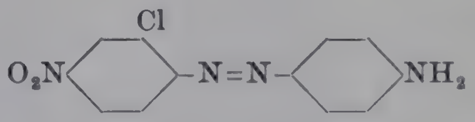
The sulfuric acid colors of amino- and hydroxyazo dyes not containing sulfonic groups are similar to those of the parent azo compounds of the benzene, naphthalene or mixed benzene-napththalene series; but the introduction of one or more sulfonic groups alters the colorations in a manner not yet correlated with the constitution of the dyes.

[121a] For an account of azo dyes as indicators, see Kolthoff, *Anal. Chem.* **22**, 65 (1950).

Fission of the azo linkage. Fission of the azo linkage by reducing agents, resulting in decolorization, is a characteristic property valuable for the detection and estimation of azo dyes and for the determination of their constitution; and in dyeing and printing for the destruction of the dyes when this is desired. When a monoazo dye is reduced the products are (*a*) the primary amine, the diazonium salt of which was used in preparing the dye; and (*b*) an amino derivative of the second component, the position of the amino group indicating the point of attachment of the diazo group.



If the dye contains a nitro group, this usually is also reduced. Nitro groups can be preferentially reduced to amino groups by aqueous sodium sulfide (NaHS to Na_2S_x), leaving the azo groups intact. Control of temperature and time of heating is necessary. Side reactions can be diminished by adding sodium chloride.[122] Such preferential reduction is used technically in the preparation of aminoazo dyes. The azo group in an azo compound such as (I) containing a nitro group can be preferentially reduced by



(I)

dissolving in alcohol, heating on the waterbath and adding slowly a solution of stannous chloride in concentrated hydrochloric acid.[123] The quantity of stannous chloride has to be carefully controlled. The method can be used for azo dyes containing sulfonic groups by converting them first into the diphenylguanidine salts that are soluble in alcohol. Distillation with sodium dihydrogen phosphate also reduces an azo group, leaving a nitro group unaffected.

The structure of an azo dye can be determined by isolation and characterization of the reduction products,[124] but the experimental problem is difficult and complicated when a polyazo dye is under examination. The number of the products, their similarity, and their ready oxidizability render separation less easy with increasing complexity of the dye. A variety of reducing agents may be employed: neutral or alkaline hydrosulfite; tin or stannous chloride and hydrochloric acid; titanous chloride; zinc dust and caustic soda; glucose and caustic soda; Raney nickel.[125] Distillation of azo dyes with soda lime results in the hydrolytic fission of the azo group, provided the dyes contain groups which can form a salt with the alkali. The products are the corresponding arylamines, except that a sulfonic group may be eliminated.[126] In attempting to isolate all the products of reduction, it is often convenient to carry out separate reductions under two or three different conditions. Forster and Hanson[127] have described procedures for the reduction of azo dyes by means of acid stannous chloride and neutral hydrosulfite, and have evolved a scheme, based on color reactions and spot tests, for the identification of the naphthalenoid reduction products. Color reactions are often inadequate for distinguishing between closely related products like amino-J-acid and amino-γ-acid, and Fierz-David has used the spectroscopic method.[128] The products of reduction cannot in all cases differentiate between two dyes of closely related structures; the constitution has then to be confirmed by synthesis and careful comparison of the dyeing properties and absorption spectra of the synthetic dyes of authentic constitution with those of the commercial dyes. An example is Columbia Black FF extra which possesses the constitution (I)[129] and to which CI 539 assigns the constitution (II). Identical products of reduction will be obtained in either case. In the preparation of Columbia Black FF,

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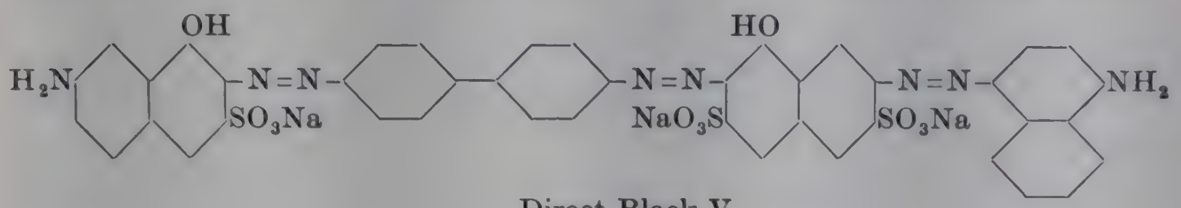
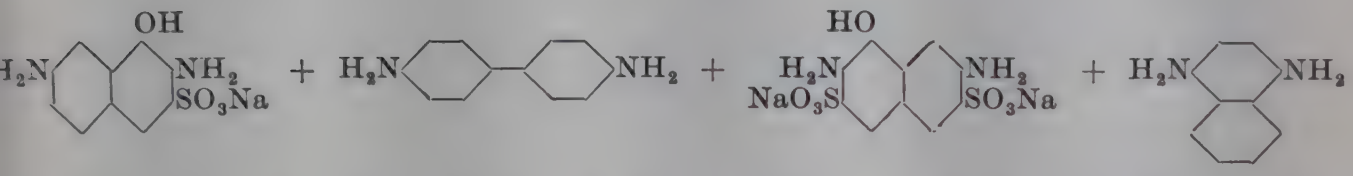
[122] Rossander, USP 2,199,576.

[123] *FIAT* 1313, III.

[124] Brunner, Analyse der Azofarbstoffe, Springer, Berlin, 1929; Green, The Analysis of Dyestuffs, Griffin, London, 1915.



Direct Black V



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[125] Whitmore and Revukas, *JACS* **59**, 1500 (1937).

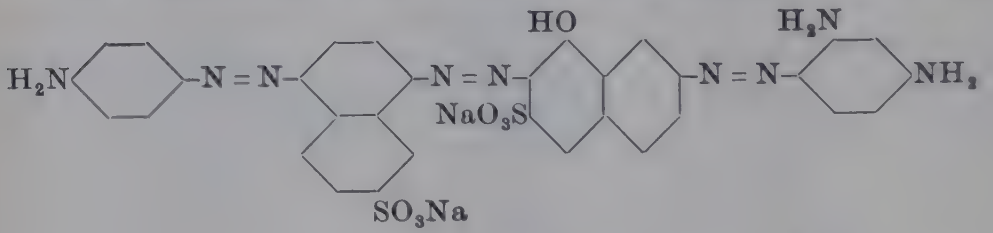
[126] Cross, *J. Soc. Dyers Colourists* **61**, 74 (1945).

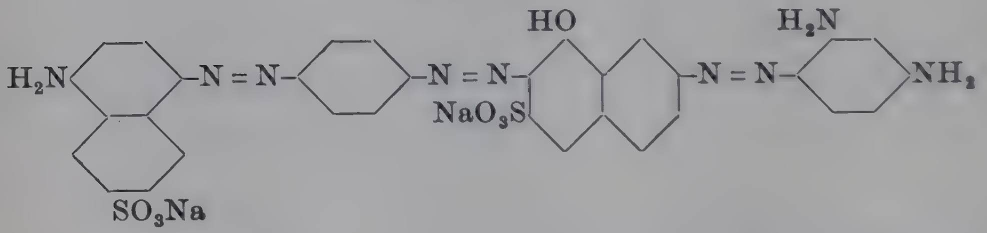
[127] *Ibid.* **42**, 272 (1926); see also Ping Chen and Cross, *ibid.* **59**, 144 (1943).

[128] *Ibid.* **45**, 133 (1929); Fierz-David, Künstliche Organische Farbstoffe, Springer, Berlin, 1926, p. 657.

[129] *Ibid.* p. 164; Rowe, The Development of the Chemistry of Commercial Dyes. Institute of Chemistry, London, 1938, p. 25.

the monoazo dye (III) is first prepared, and this diamine is monodiazotized and coupled under alkaline conditions with the monoazo dye obtained by coupling diazotized γ-acid with *m*-phenylenediamine; it has been shown that in (III) the amino group in the naphthalene residue diazotizes more readily, so that (I) is the correct constitution. It should be added however that (I) merely represents the essential constituent of the commercial dye, since it is obvious from the nature of the reactions involved that the final product will not be a single substance.


(I)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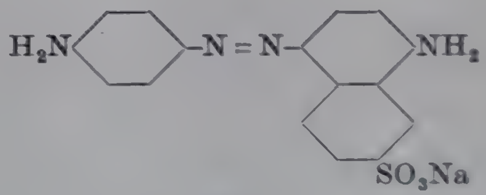
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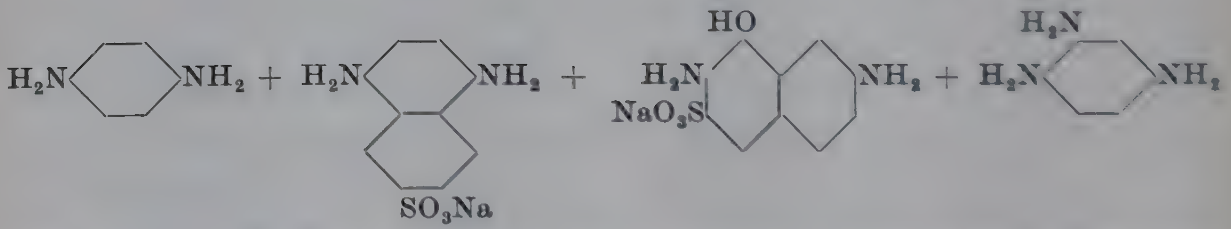

Boiling mineral acids can be used for cleaving the azo group; during this fission, in contrast to the reduction of azo dyes by hydrosulfite and alkali, a nitro group is not reduced.[130]

Commercial azo dyes being standardized products, and not chemically pure individual compounds, constitutional problems become further complicated because of the diluents added by the dye manufacturer, in addition to the by-products of the series of reactions involved in the manufacture of the dye. When the extraneous substances are inorganic and non-tinctorial constituents, the dye may be examined without purification. When two or more dyes have been mixed for shading or standardization purposes, these have to be separated. Difficulties in separation are enhanced by the similarity of the substances to be separated and by the fact that the dye manufacturer naturally chooses for admixture dyes with similar solubilities and rates of dyeing. Considerable experimental ingenuity is therefore necessary for the isolation of the component dyes in pure form. Chromatographic adsorption methods have received some attention.[131]

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[130] Rowe and Dangerfield, *J. Soc. Dyers Colourists* **52,** 48 (1936); see also Ref. 108.

For the preparation of an azo dye in analytically pure form, the usual method is to precipitate the saturated aqueous solution with sodium or potassium acetate, filter and dry the mixture of dye and acetate, and extract the latter with absolute alcohol. The process is repeated several times, until no physical or chemical evidence of impurities can be obtained and the elementary analysis gives constant values. If the alkalinity of sodium and potassium acetate leads to a considerable increase in the solubility of the dye, ammonium bromide may be used.[132]

Azo dyes can be purified by means of diphenylguanidine or di-*o*-tolylguanidine.[133] If a solution of the hydrochloride is added to a hot solution of the dye, a tarry precipitate is formed at once and can be collected on a glass rod. It solidifies on cooling, and is then broken up, washed with water containing a little of the guanidine hydrochloride, and dissolved in methanol. The dye is then isolated as the sodium salt by adding the theoretical amount of sodium hydroxide. Some of the guanidine salts can be recrystallized from absolute or aqueous alcohol.

Azo dyes may be freed from electrolytes by dialysis, the dye being obtained as a mixture of the free acid and the sodium salt.[134]

The value of absorption spectra in assessing the purity of commercial dyes is exemplified by Brode's work on Naphthol Blue Black (*p*-nitroaniline $\xrightarrow{\text{1. acid}}$ H-acid $\xleftarrow{\text{2. alk.}}$ aniline), which is an important acid color and the basis of most of the commercial acid blacks. The impurities likely to be present in it are the two monoazo dyes and the disazo dye (*p*-nitroaniline, 2 moles $\rightrightarrows$ H-acid). By determining the absorption spectra of the pure dyes, Brode developed a spectrophotometric method for standardizing Naphthol Blue Black (Agalma Black 10B) and for the quantitative determination of the impurities. He also obtained data regarding the mechanism and reactions of mixed dyeings with azo colors.[135]

The quantitative estimation of azo dyes is generally carried out by Knecht's titanous chloride method.[136] A modification of the method for the estimation of nitro compounds and azo dyes is to add sodium citrate and sodium bicarbonate to the solution of the substance, treat with a slight excess of titanous chloride and titrate the excess titanous salt with ferric alum.[137]

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[131] See Chapter XLII.

[132] Hartwell and Fieser *OSCV* II, p. 149.

[133] Rose, *Ind. Eng. Chem.* **25,** 1028 (1933); Rose and du Pont, USP 1,674,128; see also Lenher and Smith, *JACS* **57,** 497 (1935).

[134] Schramek and Götte, *Kolloid-Beihefte* **34,** 218 (1931).

[135] *Ind. Eng. Chem.* **18,** 708 (1926).

[136] Knecht and Hibbert, New Reduction Methods in Volumetric Analysis, 2nd ed., Longmans, London, 1925.

THE COLOR OF AZO DYES

The empirical facts are reviewed in some detail in order to facilitate an understanding of the constitutional variations adopted by the dye chemist and manufacturer for the production of dyes with specific tinctorial and dyeing properties.[8, 138] With the azo group as the characteristic chromophore, the possible variations which influence the color and the dyeing properties are (*a*) the number and position of the azo groups; (*b*) the nature of the aromatic nuclei—benzene, naphthalene, pyrazolone; (*c*) the nature, number and position of substituents such as halogen, alkyl, amino, hydroxyl alkoxyl and nitro groups, and (*d*) the number and position of the sulfonic groups.[139] It is obvious that various combinations of these factors can be utilized for obtaining a given effect, and that the color of the dye will ultimately depend on the constitution of the molecule as a whole. In the choice of components for a commercial dye of a desired shade, the cost and accessibility of the intermediates and the coupling conditions have to be considered.

Monoazo dyes. Some coupling components for monoazo dyes are listed in Table I, arranged in order of increasing depth of hue of the azo dyes derived from them. The first column in Table I gives the diazonium components, and the second column the second components. Components at the top of the table, when coupled with each other, yield yellow shades; in the middle of the table, reds and browns; at the bottom of the table, blues. Diazonium components at the top of the Table coupled with second components at the bottom, and *vice versa*, will give intermediate shades. For several reasons, the order of increasing depth of color in either column is only a broad indication. A diazonium component at one point in the scale, coupled with two second components, might give a deeper color with the second component occupying a higher position in the column, since the color of the dye depends on the constitution of the entire dye molecule (the auxochromophoric system). The shades which have been considered in arranging the intermediates in Table I are the direct shades on wool; with intermediates such as 1-amino-2-naphthol-4-sulfonic acid and chromotropic acid, the application of the dyes with the aid of metallic mordants will lead to a profound alteration in the shades. These limitations notwithstanding, Table I gives a useful idea of the colors obtainable by the combination of specific intermediates. Examples are the use of salicylic

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[137] Kolthoff and Robinson, *Rec. trav. chim.* **45**, 109 (1926).

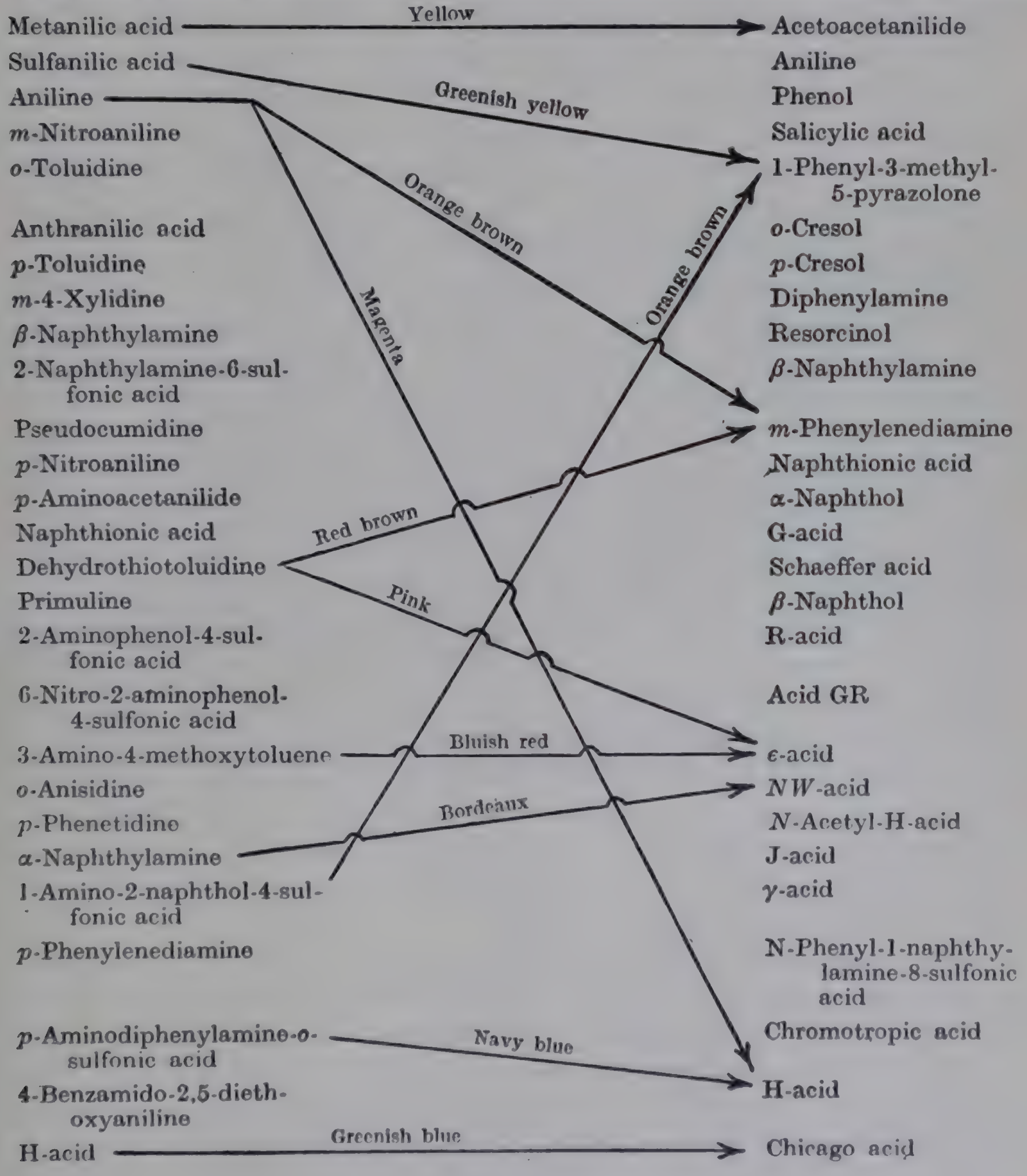
[8] See p. 413.

[138] See Chapter XLI.

[139] See also Reynolds, *Am. Dyestuff Reptr.* **32**, 455 (1943).

TABLE I

COUPLING COMPONENTS FOR MONOAZO DYES IN ORDER OF INCREASING DEPTH OF HUE



Diazonium component	*Second component*
Metanilic acid	Acetoacetanilide
Sulfanilic acid	Aniline
Aniline	Phenol
m-Nitroaniline	Salicylic acid
o-Toluidine	1-Phenyl-3-methyl-5-pyrazolone
Anthranilic acid	*o*-Cresol
p-Toluidine	*p*-Cresol
m-4-Xylidine	Diphenylamine
β-Naphthylamine	Resorcinol
2-Naphthylamine-6-sulfonic acid	β-Naphthylamine
Pseudocumidine	*m*-Phenylenediamine
p-Nitroaniline	Naphthionic acid
p-Aminoacetanilide	α-Naphthol
Naphthionic acid	G-acid
Dehydrothiotoluidine	Schaeffer acid
Primuline	β-Naphthol
2-Aminophenol-4-sulfonic acid	R-acid
6-Nitro-2-aminophenol-4-sulfonic acid	Acid GR
3-Amino-4-methoxytoluene	ε-acid
o-Anisidine	*NW*-acid
p-Phenetidine	*N*-Acetyl-H-acid
α-Naphthylamine	J-acid
1-Amino-2-naphthol-4-sulfonic acid	γ-acid
p-Phenylenediamine	N-Phenyl-1-naphthylamine-8-sulfonic acid
p-Aminodiphenylamine-*o*-sulfonic acid	Chromotropic acid
4-Benzamido-2,5-diethoxyaniline	H-acid
H-acid	Chicago acid

acid, 5-pyrazolones and arylamides of β-ketonic acids as second components for yellows; β-naphthol and its sulfonic acids for reds; and *m*-phenylenediamine for browns. The use as diazonium components of the simpler substituted anilines leads to yellows, oranges and reds; α-naphthylamine and its derivatives lead to violet and bordeaux shades; and H-acid leads to blues. It is important to note at this stage that the commercial monoazo dyes applied as acid colors on unmordanted wool are limited in depth of color to violet and less deep shades; a few blues are available by using H-acid as the diazonium component, but in general an increase in the number of azo groups to two or more, or the use of chrome mordant, is necessary for the production of blue, green, and black shades.

The relation between color and constitution has also been discussed in the case of azoic dyes[46] which with few exceptions contain one azo group; and in fact, empirical relationships between color and chemical constitution are more readily apparent among the azoics which belong to a single type, in contrast to the azo colors which vary widely with reference to the character, number, and position of the auxochromes.

While the characteristic chromophore in azo dyes is the azo group, the chromophoric system consists of one or more azo groups in conjunction with other chromophores—aromatic and heterocyclic ring systems, the quinone system, the nitro group, and the metal chelate group. An azo group conjugated with an ethylenic bond (–N=N–C=C–), as in the dyes obtained by coupling a diazonium salt with acetoacetanilide, is one of the modes of production of yellow dyes. Conjugation of the azo group with benzene, naphthalene and larger aromatic ring systems causes a progressive deepening of color. The replacement of a benzene by a naphthalene intermediate is the simple and common method of producing a new scale of hues; thus benzenoid azo dyes are usually yellow to red, while similar naphthalene derivatives are red, violet, blue, and black. Many *o,o'*-dihydroxyazo dyes and a few *o*-hydroxyazo dyes (particularly derivatives of 1,5- and 1,8-dihydroxynaphthalene) undergo a profound color change when they are applied to wool as acid colors, and then chromed. The chromophoric system of the dye ultimately produced on the fiber contains an azo or hydrazone chromophore in conjunction with a quinone chromophore and a chromium-containing chelate group.[115]

Dyes with more than one azo group. If arylazo groups are linked by a conjugate chain in which the resonance effects are unbroken, deepening of color ensues. The bathochromic effect is further augmented if an intervening group (such as the –NH– group) introduces the possibility of additional resonance contributions. If groups of insulating or blocking character intervene, the color effect is additive.[8] Shades deeper than the sum of the shades corresponding to the individual monoazo units in the dye molecule, but less deep than the shades of the dyes in which the azo groups are linked in unbroken conjugation, are obtained if the intervening groups do not totally insulate the resonance effects of the monoazo units. Arylazo groups in the *p*- or 1,4-positions in benzene or naphthalene are bathochromic and hyperchromic.[140, 141] Two simple examples are the yellow monoazo dye (I) and the orange disazo dye (II). Similarly, the monoazo dye (*o*-toluidine →R-acid) is scarlet, while the disazo dye (*o*-aminoazotoluene →R-acid) is bordeaux. The effect of a chain of three arylazo groups is exemplified by the bright greenish blue dye, Sirius Supra Blue 6G.[36] The multiplication of arylazo groups in this manner at 1,4-positions has two advantages: the purity and brightness of the shades when the components are suitably chosen; and the simultaneous increase in the affinity of the dye for cellulose fibers. The production of deeper hues by the multiplication of azo groups in 1,4-positions is limited by several factors. With an increase in the number of azo groups in the 1,4-positions, diazotization of the aminoazo compounds and coupling, especially the latter, become increasingly difficult. When the number of azo groups in 1,4-positions is increased to more than three, the bathochromic effect is small, in accordance with the principle of convergence discussed in Chapter VIII.

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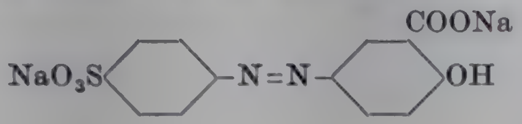
[46] See p. 430.

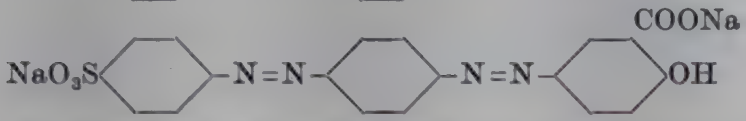
[115] See p. 445.

[8] See p. 413.

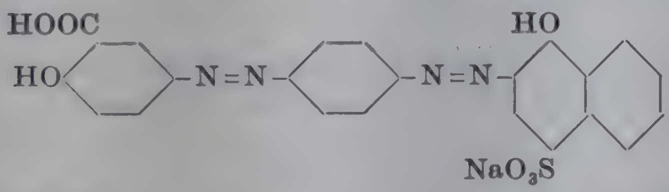
(I)



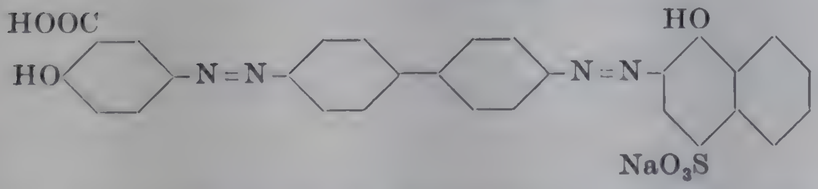
(II)



In the disazo dyes prepared from tetrazotized benzidine, which are important on account of their substantivity for cotton, there is a bathochromic effect due to the second azo group, but less than in the corresponding *p*-phenylenediamine derivatives; in other words, the separation of the two azo groups by the diphenyl nucleus has a hypsochromic effect in



(III ; Bordeaux)



(IV ; Brownish-red)

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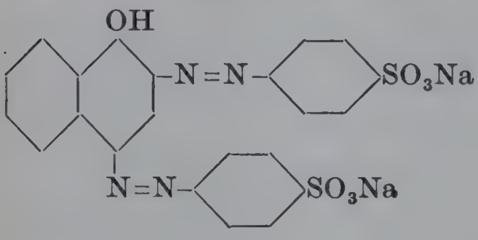
[140] For a study of the absorption spectra of such dyes, see Funkhouser and Brode, *JACS* **56,** 2172 (1934).

[141] See also Ruggli and Courtin, *Helv. Chim. Acta* **15,** 75 (1932).

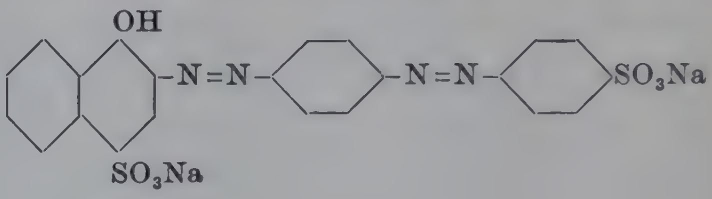
[36] See p. 428.

comparison with the benzene-*p*-disazo dyes. This will be evident from a comparison of the dyes (III) and (IV), both the shades referring to chrome-mordanted wool.

The *m*-disazo dyes obtained by coupling tetrazotized *m*-phenylenediamine with simple phenols and naphthols exhibit absorption spectra very similar to the spectra obtained by addition of the absorption bands of what might be termed the component monoazo dyes.[141] Linkage of two azo groups in the *m*- or 1,3-positions in the benzene or naphthalene ring, using relatively complex end components, tends to produce tertiary shades; the effect is neither bathochromic like the *p*-linkage nor additive as in the case of a completely insulating group such as the methylene or amide group. Disazo dyes from tetrazotized *m*-phenylenediamine are brown, olive, or black, depending on the end components. The absorption curves of polyazo dyes containing a single common auxochrome (such as the primary disazo dyes from phenol and α-naphthol) are composed of the curves of the corresponding monoazo compounds in the same solvent, but the bands are broader.[142] The dye (V) is brown, while (VI) is red.



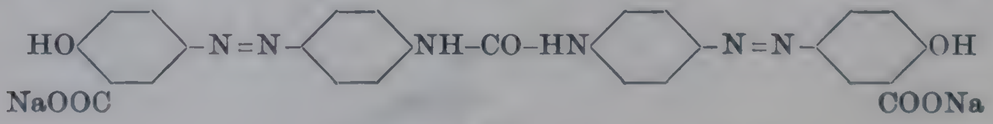
(V)



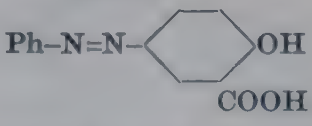
(VI)

Two azo groups in the 2,7-positions of the naphthalene nucleus have a profound effect on the depth of the color, the general tendency being towards the production of greenish or bluish blacks. Thus the monoazo dye (aniline $\xrightarrow{\text{alk.}}$ H-acid) dyes magenta, while the disazo dye (aniline $\xrightarrow{\text{alk.}}$ H-acid $\xleftarrow{\text{acid}}$ *p*-nitroaniline) is the well-known black, Naphthol Blue Black.

The next type to be considered consists of disazo and polyazo dyes in which the arylazo units are separated by various atoms and groups. The amide group, especially the urea group –NH–CO–NH–, produces a mainly additive effect; the thiourea group (–NH–CS–NH–) is similar, but offers no advantage over the urea group. The amide and urea linkages are useful



(VII)



(VIII)

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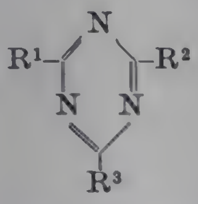
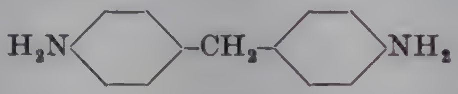
[141] See p. 455.

[142] See p. 446.

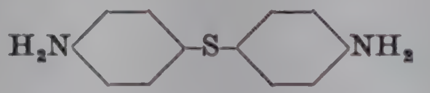
for (*a*) improving the affinity of dyes for cotton without altering the shade of a monoazo dye; and (*b*) producing mixed shades by combining two dyes. As an example of (*a*), the dye (VII) is approximately the same color as the monoazo dye (VIII), but (VII) is a useful direct cotton dye, while (VIII) will not dye unmordanted cotton. Examples of (*b*), in which green dyes result from the linking of blue and yellow dye units by means of the –NH–CO–NH– group, are cited later.[143] The triazine ring (IX) provides another method of great value for obtaining additive shades; three dye units, R¹, R² and R³, can be linked up in this manner, but it is more convenient in practice to combine two dye units R¹ and R², while R³ is a non-tinctorial group such as methoxyl or anilino. The insulating character of the triazine ring thus enables useful color combinations to be effected, e.g., green by the use of a blue dye unit for R¹ and yellow for R².

(IX)





(X)



(XI)

The methylene group is an insulator, and a disazo dye from 4,4′-diaminodiphenylmethane (X) is similar in shade to the monoazo dye from *p*-toluidine,[138, 144] but the former leads to acid colors with greatly improved fastness to severe washing treatments. The sulfide linkage has a somewhat similar effect on color and fastness, and the disazo dyes from thioaniline (XI) are comparable to the similarly constituted dyes from (X).

Disazo dyes from 4,4′-diaminostilbene-3,3′-disulfonic acid are deeper and more intense in color than the benzidine analogs.[144] The stilbene azo dyes are also notable for their fastness to light and affinity for cotton.[145] Disazo dyes from 4,4′-diaminodiphenylamine are much deeper in color than the corresponding benzidine dyes; the bathochromic effect is more pronounced than that of the –CH=CH– linkage, and is more complex in character. The tendency is for the production of drab tertiary shades, and since the substantivity for cotton, which is characteristic of the benzidine dyes, is retained in the dyes from diaminodiphenylamine, its main use is for the production of blacks; three azo groups are usually necessary to produce the requisite color value and fastness.

The effect of auxochromes. Hydroxyl and amino groups play a vital role in influencing the color and dyeing properties of azo dyes. Electronic interaction between chromophore and auxochrome is especially facile in an azobenzene chromophoric system carrying hydroxyl or amino groups. The sensitivity of some azophenols to alkali and of aminoazobenzene derivatives to acid is an example of the influence of the auxochrome not only on the color of azo dyes, but also on their fastness to wet treatments. Halogen, alkyl, alkoxy, acylamido and nitro groups are used to modify the hue and other properties associated with particular hydroxyarylazo and aminoarylazo systems. The position of the substituent with reference to the azo group largely determines the auxochromic effect; since resonance effects are inoperative in the *m*-position, substituents are mainly effective in the *o*- and *p*-positions, particularly in the *p*-position on account of the lengthening of the conjugated chain and the absence of steric hindrance to coplanarity. The latter effect is noticeable in the case of the chlorine atom (and of still heavier atoms and groups) in the *o*-position, so that such *o*-substitution is hypsochromic. A substituent *meta* to the azo chromophore can exercise a bathochromic effect, although it is usually weak, if it is oriented *para* to a second auxochrome. Thus cresidine (I) and 4-chloro-*o*-anisidine (II) yield slightly deeper hues than *o*-anisidine; and 2,5-dimethoxyaniline leads to dyes of bluer shade than *o*-anisidine.

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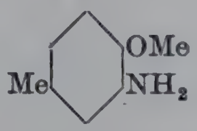
[143] See Chapter XVI.

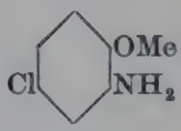
[138] See p. 452.

[144] Piper and Brode, *JACS* **57**, 135 (1935); *ibid.* **63**, 1502 (1941).

[145] See Chapter XX.

(I)

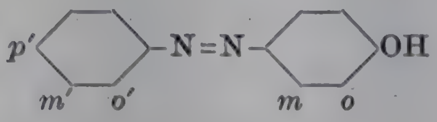




(II)

While *p*-chlorine has a weak auxochromic effect, chlorine in the *p*- as well as in other positions sometimes increases the brightness of a dye, although to a smaller extent than alkoxyl groups; chlorine also sometimes improves the fastness to light, bleaching and acids. The influence of methyl groups is seen from the shades (orange, scarlet-red, bluish-scarlet) of the three monoazo dyes obtained by coupling aniline, *m*-xylidine and Ψ-cumidine with R-acid. Increasing the size of the alkyl group does not increase the bathochromic effect, but the fastness to wet treatments is improved. Methoxyl and ethoxyl groups in *o*- or *p*-positions have a pronounced bathochromic effect towards blue, and they also increase the brightness of the shades. For technical reasons *o*-anisidine and *p*-phenetidine (and not the corresponding *p*- and *o*-isomers) are employed in the preparation of commercial azo dyes. The relative influence of Me, Cl, and OMe on the color of azo dyes is conventionally illustrated by the shades of four well-known disazo dyes obtained by coupling tetrazotized benzidine, *o*-tolidine, dichlorobenzidine and dianisidine with naphthionic acid: Congo Red (red), Benzopurpurine 4B (scarlet), Dianol Red 2B (bluish red) and Benzopurpurine 10B (carmine-red).

Our knowledge of the influence of substituents on the absorption spectra of azo dyes is mainly due to Brode,[146, 147] who has examined a series of azophenols (III) substituted by Me, Cl, Br, I, or NO_2 in either or both



(III)

the rings. The position and intensity of the absorption bands were determined in three solvents: 95% alcohol, concentrated hydrochloric acid, and 3% aqueous sodium hydroxide. From his data, Brode arrived at the following generalizations: (1) An increase in molecular weight is usually accompanied by a decrease in frequency of the absorption bands. This decrease is roughly proportional to the increase in molecular weight, but varies with the position of substitution. (2) Substitution in the *p*′-position by NO_2, Me, or halogen produces a maximum in the magnitude of the absorption bands in all solvents. In alcohol, the only solvent for which complete information is available, the order of magnitude is $CH_3 < Cl < Br < I < NO_2$. (3) Substitution of halogen atoms in the *o*′-*o*-positions in the disubstituted compounds produces a very marked decrease in the magnitude of the absorption bands in all solvents. (4) In the disubstituted compounds the increases or decreases of magnitude of the absorption bands bear little mathematical relation to the effects produced by the constituent groups separately. (5) In the *p*′-*o*-disubstituted compounds the *p*′-substituent seems to exert a stronger influence on the frequency of the absorption maximum in alcohol, while the *o*-substituent has more effect on the extinction of the absorption band. In hydrochloric acid and sodium hydroxide there is little relation between effect and position. (6) In all solvents, the extinction of the absorption band for a given bromo compound is either equal to or slightly greater than that of the corresponding chloro compound, regardless of position of substitution. (7) The principal absorption bands of these compounds in sodium hydroxide appear to consist of two overlapping bands, which are believed to be due to two forms of vibration of the molecule, present in equilibrium. Analysis of these compound bands into their components gives information concerning the effect of position isomerism on this equilibrium. The chloro derivatives appear to exist in four equilibrium levels, whereas the bromo derivatives appear to exist in six levels. (8) The sums of the extinction of the components of the

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[146] Brode, *Ber.* **61**, 1724 (1928); *Bur. Standards J. Research* **2**, 501 (1929); *JACS* **51**, 1204 (1929); **56**, 1037 (1934); Proceedings of the Sixth Summer Conference on Spectroscopy, Wiley, New York, 1939, p. 128.

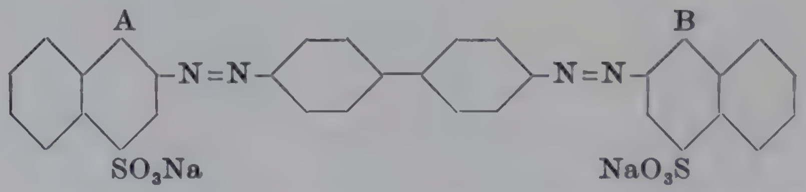
[147] See also Hodgson and Leigh, *J. Soc. Dyers Colourists* **57**, 82 (1941).

principal absorption band in sodium hydroxide solution appear to bear general relationships to the positions of substitution, whereas the extinction values of the separate components seem to show little relationship.[148]

Blumberger[149] has examined the absorption spectra of *o*-hydroxyazo dyes of the type (A ⟶ R-acid) in which A was aniline or aniline substituted by Me, OMe, NH_2, NHAc, Cl, NO_2, COOH and SO_3H. A bathochromic effect was parallel to an increased fastness to alkali, i.e., a decreased tendency to dissociation of OH.

The primary amino group is an important auxochrome. One example of its auxochromic effect is that the dye (aniline ⟶ chromotropic acid) dyes bluish-red as an acid color on unmordanted wool, while the *p*-phenylenediamine analog dyes bluish-violet. An example of the deeper color produced by the *p*-aminobenzeneazo in comparison with the *p*-nitrobenzeneazo system is the change in color of Chromotrope 2B (*p*-nitroaniline ⟶ chromotropic acid) from bluish-red to violet when it is reduced to the amine. Amino groups in the naphthalene nucleus are more effective in the α- than in the β-position. 2-Azo-1-naphthylamine dyes for instance are deeper than 1-azo-2-naphthylamine dyes. The multiplication of amino groups tends to produce drab, tertiary shades, and a common coupling component for browns, olives, and blacks is *m*-phenylenediamine.

The relative influence of amino and hydroxyl groups *ortho* to the azo group is exemplified by the three disazo dyes (IV); Congo Red (A and B = NH_2) is red; Congo Corinth (A = NH_2; B = OH) is brownish violet; and the dye (A and B = OH) is red-violet.



(IV)

Acylation of the amino group diminishes its auxochromic effect; cf. the red monoazo dye (aniline $\xrightarrow{\text{alk.}}$ acetyl-H-acid) with the bluish-red monoazo dye (aniline $\xrightarrow{\text{alk.}}$ H-acid). It must be noted, however, that an acylamido group has definite auxochromic properties; for instance, *p*-aminoacetanilide and 2,5-diethoxy-4-benzamidoaniline (Fast Blue BB Base) as diazonium components give bluer dyes than the corresponding amines not containing an acylamido group. Acylamido groups (e.g., chlorobenzamido and *p*-toluenesulfonamido groups) also improve the purity of the tone and the fastness properties.

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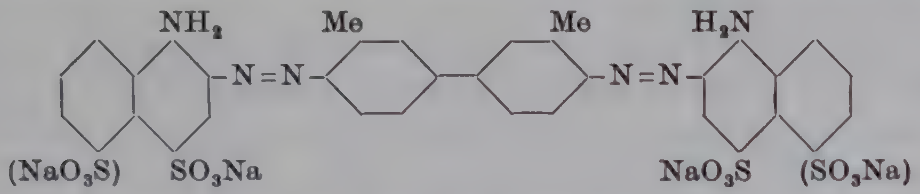
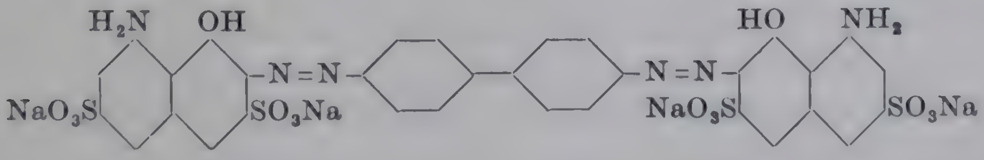
[148] Brode and Cheyney, *J. Org. Chem.* **6**, 341 (1941).

[149] *Rec. trav. chim.* **59**, 665 (1940); **63**, 127 (1944) and other papers.

Secondary and tertiary amino groups are more effective auxochromes than the primary amino group.[150] The dyes obtained by coupling diazotized sulfanilic acid with aniline, dimethylaniline and diphenylamine are yellow, orange-yellow and orange respectively. The phenylamino and *p*-tolylamino groups are powerful auxochromes. Coupling aminoazobenzenedisulfonic acid with β-naphthylamine and with *p*-tolyl-β-naphthylamine, the first dye is scarlet and the second black.

The effect of the sulfonic group on color. With the exception of the insoluble azo colors which are classified and treated separately as azoic dyes, and of a few dyes such as the azosalicylic acids and the basic colors, all azo dyes contain one or more sodium sulfonate groups (SO_3Na). The primary function of the sulfonate group is to render an azo dye water-soluble and the influence on the color of azo dyes is of a minor character. The influence of the position of the sulfonic group is illustrated by Benzopurpurine 4B (I) and 6B (the sulfonic groups are in the 5,5′-positions, shown within brackets). As indicated by the suffixes 4B and 6B, the latter dyes a bluer shade, so that the presence of a sulfonic group in the same ring as the auxochrome and the azo linkage has a hypsochromic effect in comparison with sulfonation in the unsubstituted ring. Dyes derived from H-acid and Chicago acid represent similar examples; (II) is reddish-blue and (III) greenish-blue.[151] It would appear that proximity to the azo group is the significant factor in the hypsochromic effect of the sulfonic group; this is apparent from an inspection of the structures of the orange dyes (IV and V) derived from G-acid and R-acid; (IV) in which the


(I)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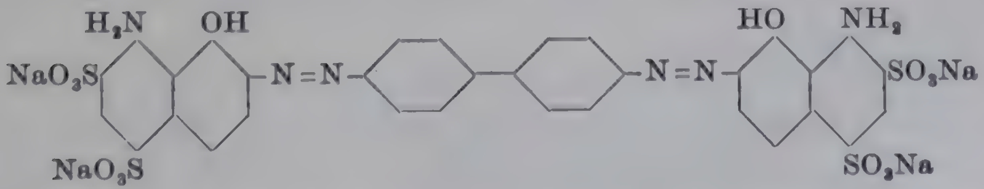
(III)

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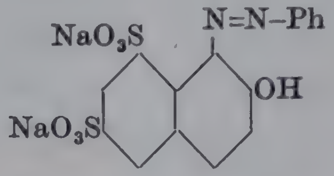
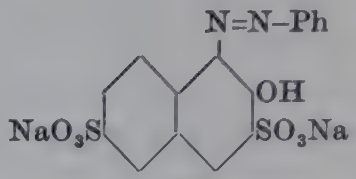
[150] For the absorption spectra of certain carcinogenic aminoazo dyes, see J. A. Miller, Sapp and E. C. Miller, *JACS* **70**, 3458 (1948).

[151] Fierz-David, Künstliche Organische Farbstoffe, Ergänzungsband, Springer, Berlin, 1935, p. 5.

benzeneazo group and the sulfonic group are in the *peri*-positions is orange-yellow, while (V) is reddish-orange.

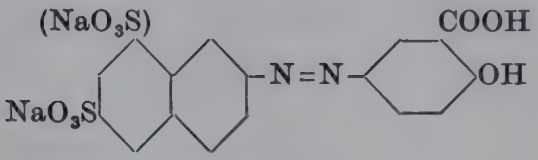
(IV)



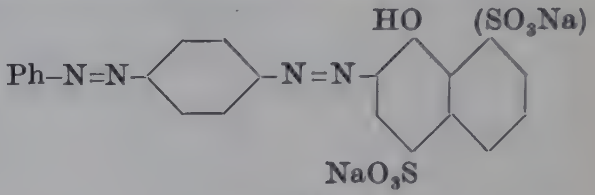


(V)

The effect of introducing a second sulfonic group is seen in pairs of



(VI)



(VII)

dyes such as (VI), in which the monosulfonated compound dyes red-yellow on unmordanted wool, and the disulfonate yellow; and (VII) in which the respective shades are red and scarlet.

Brode and Griffith[152] have determined the absorption spectra, the dyeing and exhaustive properties, and the washing and light fastness, of a series of monoazo dyes obtained by coupling diazotized aniline and its three sulfonic acids with naphthols, naphthylamines and their sulfonic acids. Both the naphthol and naphthylamine series showed the lowest frequency of the primary band when the sulfonic group was in the 8-position, and the highest frequency in the 2-position. In the 2-azo-1-naphthylamines and 1-naphthols, moving the sulfonic groups to positions 3, 4 and 5 gradually decreased the frequency, although the effect was small. The frequencies of the principal maxima of monoazo dyes prepared by coupling diazotized aniline (A), sulfanilic acid (S), metanilic acid (M) and orthanilic acid (O) with β-naphthol (β) and its 5-, 6- and 7-sulfonic acids (marked 2,5-, 2,6- and 2,7) are represented in Fig. 1. The length of the lines indicates relative intensity of the absorption band. Lines pointing upward represent maxima observed in water as solvent; downward lines represent maxima in hydrochloric acid solution.

While Meuly[153] and Dinner,[154] who examined many disazo and trisazo dyes for their absorption spectra in the visible region, have reported that the introduction of sulfonic groups produced a bathochromic effect, and that *p*-substitution was more effective than *o*- or *m*-, somewhat different results were obtained by Brode and Eberhart[155] in their more systematic investigation of 48 dyes of the benzeneazo-1- and 2-naphthylamine series containing not more than one sulfonic group in each of the aryl nuclei. The sulfonic group had a definite effect on the absorption spectra, the nature of which depended on the orientation of the amino, azo and sulfonic groups. Sulfonic groups in the second component usually produced a hypsochromic effect, which was greatest for dyes from 1-naphthylamine-2-sulfonic acid; the only exception, in which the effect was bathochromic, was 1-naphthylamine-8-sulfonic acid. Introduction of sulfonic groups into the diazonium component always produced a bathochromic effect, but the quantitative effect in relation to the orientation of the sulfonic group in the *o*-, *m*- or *p*-position with reference to the azo group differed according as the second component was an α- or β-naphthylamine derivative; with α-naphthylamine the order of decreasing bathochromic effect was $p > m > o$, but for β-naphthylamine the order was $o > p > m$. Intensity of absorption followed the same general trends as frequency. Brode and Eberhart further observed that the 2-azo-1-naphthylamine dyes exhibited absorption curves in neutral solution in which the frequencies of the three principal maxima were consistently 2, 3 and 4 times that of a fundamental frequency of 310 to 330 fresnels.

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[152] *Am. Dyestuff Reptr.* **26**, 90 (1937).
[153] *Helv. Chim. Acta* **6**, 931 (1923).
[154] *Z. angew. Chem.* **41**, 1078 (1928).
[155] *J. Org. Chem.* **5**, 162 (1940).

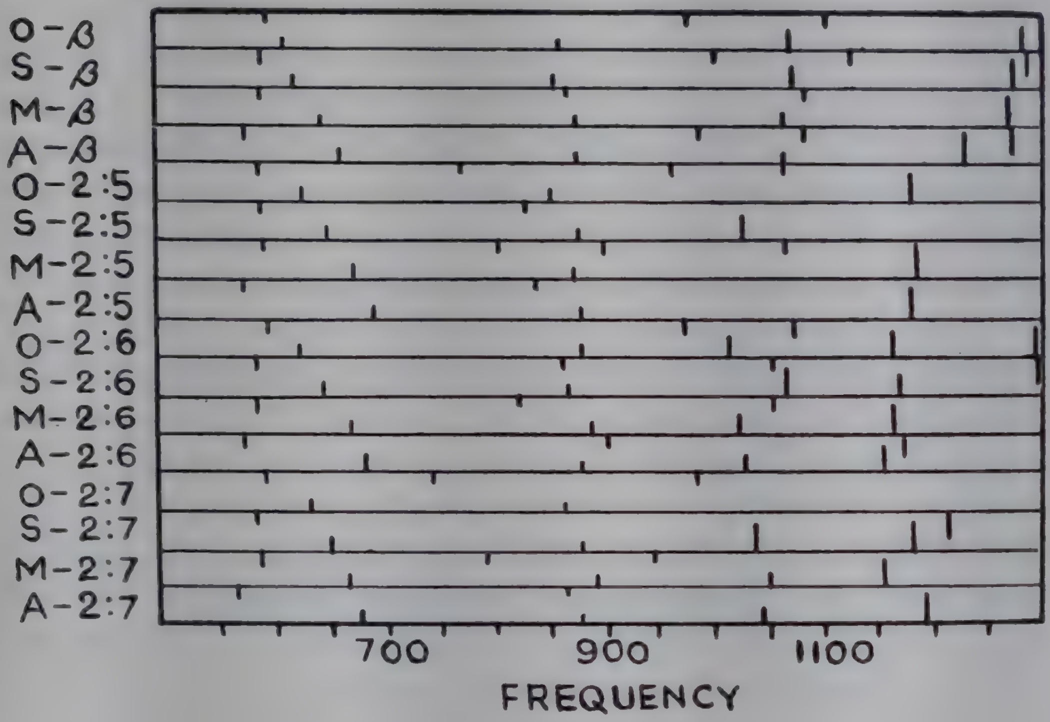

Fig. 1 (Brode and Eberhart).

CLASSIFICATION OF AZO DYES

Because of the very large number of azo dyes, possessing structures of varying complexity and different dyeing properties, a somewhat detailed subdivision has been included in the main classification of dyes (Chapter V). The division of the azo dyestuff class into smaller groups, adopted in the following treatment, takes into account (*a*) the number of azo groups; (*b*) the presence of characteristic ring systems; (*c*) the order of the series of coupling reactions; and (*d*) special dyeing properties. The insoluble azo dyes, inclusive of those applied to textiles and of the pigments used for other purposes, are grouped together as azoic dyes and treated separately.

Symbols. The classification of the dyes containing more than one azo group is partly based on the methods of preparation, and it is necessary to expand the exposition made earlier in this chapter. With one or more coupling reactions as the common factor, the mode of representation has to specify the intermediates, the order in which the coupling reactions are carried out, and if an intermediate can direct an entering azo group into one of two positions, the acidity or alkalinity of the medium on which this is dependent. In dealing with individual dyes, the intermediates are named, but for the purposes of classification and the treatment of groups of dyes, the intermediates are divided into six types representing six distinct functions in the scheme of preparation.

Five of these six types of intermediates are denoted by the symbols adopted by Lapworth;[156] T is an additional symbol.

A is an aromatic amine (first or diazonium component) which is diazotized and coupled with a second component; if several such amines are used, they are represented as A^1, A^2, etc.

D is a diamine (such as benzidine) which is tetrazotized and coupled with two moles of the same or different second components. With two moles of the same component, the scheme of preparation may be written as $\mathrm{D} \rightrightarrows \mathrm{E}_2$.

E is a second component, a phenol or amine with which a diazonium salt is coupled; it is further characterized by the fact that it is not submitted to any additional treatment in a coupling reaction. In a monoazo dye, therefore, it is the second component, and in a polyazo dye it is the end component with which the final coupling of a diazonium salt is carried out. If two different end components are used, they are represented as E^1 and E^2.

Z is a second component such as H-acid, which has two coupling positions and which may therefore be coupled with two moles of the same diazonium salt or one mole each of two different diazonium salts. In the former case, the dual coupling may be represented as $A_2 \rightrightarrows Z$.

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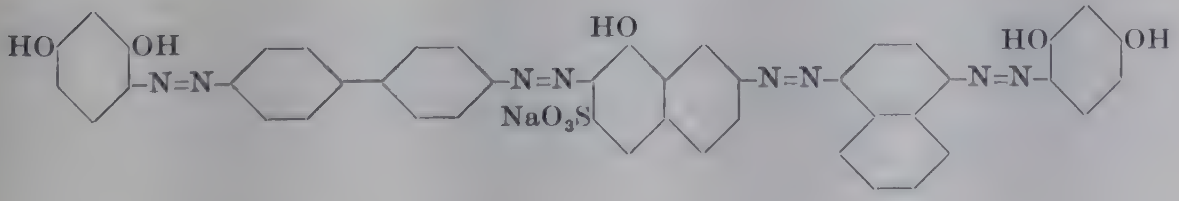
[156] Thorpe's Dictionary of Applied Chemistry, 4th ed., Vol. IV, Longmans, London, p. 195; cf. Winther, Zusammenstellung der Patente auf dem Gebiete der organischen Chemie, Band II, Organische Farbstoffe, Topelmann, Giessen, 1908, p. 1191.

T is a second component which has three coupling positions and can be coupled with three moles of diazonium salts; an example is *m*-phenylenediamine. The third coupling is usually carried out on the fiber, and it is doubtful if it goes to completion.

M represents a middle component; this is a primary aromatic amine which is used in the first instance as a second component for coupling with a diazonium salt. The coupling takes place in such a position that the amino group remains diazotizable, so that the monoazo dye can now be used as a diazonium component and coupled with an end component to form a disazo dye. In the benzene series a middle component is aniline or a nuclear substituted derivative with a free *p*-position in which coupling can take place; in the naphthalene series it is either an α-naphthylamine with the 4-position free for coupling, or a primary amine, such as γ-acid, in which coupling is effected in the ring not carrying the amino group to be diazotized.

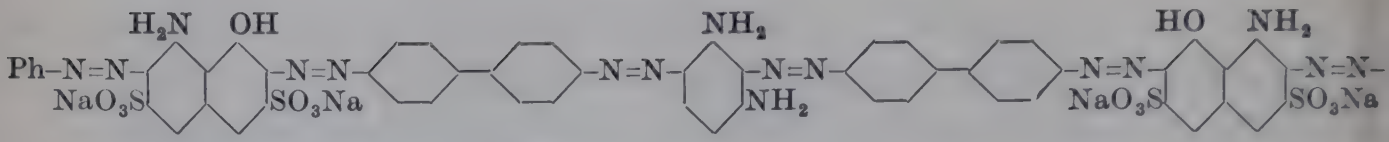
The same intermediate may perform two or more different functions in the preparation of the same or different dyes, and it will therefore bear different symbols. Aniline, for instance, is diazotized and coupled with itself for the production of aminoazobenzene, so that it is both A and E in the scheme A→E. H-acid can be used as the primary amine for diazotization and coupling with a second component; it can be coupled first with a diazonium salt and the amino group in the monoazo dye can then be diazotized and coupled; and as a second component, H-acid can couple with one or two moles of a diazonium salt. H-acid can therefore function as A, E, M or Z.

Two examples are quoted in illustration of the system for representing the constitution and preparation of azo dyes. One is a tetrakisazo and the other a hexakisazo dye, and for each the structural formula, the general scheme of preparation, and the scheme specifying the intermediates are stated.



$$E \xleftarrow{3} D \xrightarrow{1.\ \text{alk.}} M^1 \xrightarrow{2} M^2 \xrightarrow{3} E$$

$$\text{Resorcinol} \xleftarrow{3} \text{Benzidine} \xrightarrow{1.\ \text{alk.}} \gamma\text{-Acid} \xrightarrow{2} \alpha\text{-Naphthylamine} \xrightarrow{3} \text{Resorcinol}$$



$$(\mathrm{A} \xrightarrow{\text{1. acid}} \mathrm{Z}^1 \xleftarrow{\text{2. alk.}} \mathrm{D})_2 \overset{3}{\rightrightarrows} \mathrm{Z}^2$$

$$(\text{Aniline} \xrightarrow{\text{1. acid}} \text{H–Acid} \xleftarrow{\text{2. alk.}} \text{Benzidine})_2 \overset{3}{\rightrightarrows} m\text{–Phenylenediamine.}$$

Azo dyes are treated in the sequel in accordance with the following classification, in which the main intermediates, the colors of the dyes and the applications are indicated:

I—Monoazo dyes (A⟶E). (1) A and E are benzene or naphthalene derivatives, containing SO_3H; E may be a pyrazolone; yellow to blue dyes for wool. (2) E is *m*-phenylenediamine; a few brown basic dyes for cotton.

II—Mordant dyes. (*a*) Azosalicylic acids. (*b*) *o,o′*-Dihydroxyazo dyes. (*c*) Preformed soluble coordination complexes. Full range of shades; all are wool dyes.

III—Disazo dyes. (*a*) Primary ($A^1 \longrightarrow Z \longleftarrow A^2$): (1) Z is resorcinol or *m*-phenylenediamine. Limited range of brown dyes for leather and wool. (2) Z is H-acid. Small but very important group of blue-black acid dyes. (3) Z is carbonyl-J-acid. Scarlet to red direct cotton dyes. (*b*) Aminoazobenzene and naphthalene derivatives: (A⟶M⟶E). (1) A, M and E are benzene and naphthalene derivatives suitable for the two coupling reactions; red, violet, blue and black acid dyes. (2) E is J-acid or one of its derivatives; red to violet direct cotton dyes. (3) E is γ-acid; grey to black direct cotton dyes. (*c*) Derivatives of tetrazotized diamines ($E^1 \longleftarrow D \longrightarrow E^2$): (1) D is benzidine or similar *p*-diamine derivative; direct cotton dyes of all shades except green; a few applicable to wool. (2) D is a *m*-phenylenediamine derivative; E^1 and E^2 are *m*-phenylenediamine or a derivative; a very small group of direct and basic dyes for cotton. (3) D is a *m*-substituted benzidine or other 4,4′-diamine not yielding direct cotton dyes; D may be benzidine, if E^1 or E^2 is a suitable phenol, naphthol or pyrazolone; orange to red acid dyes.

IV—Trisazo dyes. In the sub-divisions indicated below for polyazo dyes, the sequence of the diazotization and coupling reactions is variable.

Trisazo and tetrakisazo dyes are essentially direct cotton dyes; a few are useful leather dyes. T is resorcinol or *m*-phenylenediamine or one of

(*a*)
$$\begin{tikzcd}
A^1 \arrow[r] & T & A^2 \arrow[l] \\
& A^3 \arrow[u] &
\end{tikzcd}$$

their derivatives. Brown leather dyes may be prepared, but they are not of practical importance.

(*b*) $A \longrightarrow M^1 \longrightarrow M^2 \longrightarrow E$. M^1 is aniline or α-naphthylamine or a derivative with a free *p*-position; M^2 is usually Cleve acid or 2-ethoxy-Cleve acid; E is J-acid or a derivative; series of important blue and green dyes.

(*c*) $E^1 \longleftarrow D \longrightarrow M \longrightarrow E^2$. D is benzidine or a derivative or *p*-phenylenediamine; M is α-naphthylamine or γ-acid; and E^2 is *m*-phenylenediamine or a naphthol- or aminonaphtholsulfonic acid; blue, brown and black dyes.

(*d*) $A \longrightarrow Z \longleftarrow D \longrightarrow E$. D is benzidine, Z is *m*-phenylenediamine, resorcinol or H-acid, and E is phenol, salicylic acid, *m*-phenylenediamine or resorcinol; brown, green and black dyes.

(*e*) $A^1 \longrightarrow M \longrightarrow Z \longleftarrow A^2$. M is α-naphthylamine or its 6- or 7-sulfonic acid; Z is H-acid; black dyes.

V—Tetrakisazo dyes.

(*a*) $E \longleftarrow D \longrightarrow Z \longleftarrow M \longleftarrow A$

(*b*) $A \longrightarrow Z \longleftarrow D \longrightarrow Z \longleftarrow A$

(*c*) $E \longleftarrow D \longrightarrow Z \longleftarrow D \longrightarrow E$

D is benzidine or *p*-phenylenediamine or *m*-phenylenediamine; M is γ-acid; Z is H-acid, or *m*-phenylenediamine or a derivative, or resorcinol; dark brown and black dyes. Few commercial examples and more usually made on the fiber by further coupling of disazo and trisazo dyes.

VI—Stilbene dyes. Contain the stilbene chromophore in addition to one or more azo groups. Yellow, orange, and brown direct cotton dyes.

VII—Pyrazolones. Mainly yellow, and a few orange to red, acid dyes. Using appropriate intermediates in conjunction with a pyrazolone, insoluble pigments, acid mordant and direct cotton dyes can be prepared, and these are also referred to in the relevant groups of the classification.

VIII—Thiazoles. Limited range of yellow to red direct cotton dyes, some of the developing type.

IX—Urea and cyanuric acid derivatives. Mainly disazo and trisazo dyes in which azo dye units are linked together by means of urea or 1,3,5-triazine.

X—Direct cotton dyes suitable for aftertreatment on the fiber. These may also be included among the earlier groups, but are characterized by structural features, which enable them to be submitted on the fiber to one or more of several reactions, such as development with a diazonium salt or treatment with a metallic salt, in order to improve their fastness.

XI—Cellulose acetate dyes. Mainly monoazo dyes, some containing β-hydroxyethyl and similar groups, prepared in the form of aqueous dispersions suitable for application to acetate rayon. Soluble dyes contain a sulfatoethyl ($-CH_2-CH_2-O-SO_3Na$) group. Full range of shades.

XII—Azoic dyes. Insoluble dyes, mostly monoazo, prepared on the fiber, or in substance for use as pigments. In the reaction (A→E), A may be any diazotizable amine free from solubilizing groups, but only a limited number are actually used on account of shade and fastness considerations; mainly nitro-, chloro- and alkoxy-anilines and -toluidines. E belongs to two main types: (*a*) Arylamides of 2-hydroxy-3-naphthoic acid; scarlet to black shades, especially strong in reds. (*b*) Arylamides of acetoacetic acid (other β-ketonic acids are also utilizable in principle); yellow shades. In dyeing and printing, mainly applicable to cotton.

DYEING AND FASTNESS PROPERTIES OF AZO DYES

From the dyeing point of view, the water-soluble azo dyes fall into two broad classes—acid colors for wool and direct cotton dyes. Acid dyes for wool include dyes for other natural and synthetic protein and polyamide fibers such as silk and nylon, and direct cotton dyes include dyes for regenerated cellulose (or rayons other than cellulose acetate), but the dyes for these fibers have to be chosen from among the two large groups of acid and direct dyes on the basis of specific properties. While typical acid colors are unsuitable for application to cotton by a dyeing process owing to lack of affinity, direct cotton dyes are not without affinity for wool, though the number of direct cotton dyes used commercially for dyeing wool is very limited. In each of these two broad classes again, the dyes that are technically valuable are very much smaller in number than those which have been or can be prepared in the laboratory, considering the general character of the diazo coupling reaction. A dye has to fulfil many requirements regarding substantivity, leveling, fastness, suitability for routine dyeing procedures, and cost, before it can become a commercial success. Among the azo colors, dyes are available for all the textile fibers and for many non-textile purposes. From the classification and the detailed treatment of the azo colors that follows, it will be noticed that, both in the major division into mono-, dis- and polyazo dyes and in the sub-divisions depending on other structural features, the technical applicability of the dyes bears a relationship to the chemical constitution. The monoazo dyes are mainly wool colors. The disazo dyes are divisible into well-defined groups, applicable to wool, silk and leather, and to cotton and viscose. The trisazo and tetrakisazo dyes are mainly direct cotton dyes, but include some useful leather dyes. In the broad class of water-insoluble azo compounds are to be found dyes applicable to cotton when they are produced on the fiber; dyes applicable to cellullose acetate as dispersions; and pigments. Azo dyes containing basic groups, in the absence of sulfonic groups, are basic dyes, applicable to cotton on a tannin mordant, but there are few dyes of technical value belonging to this type.

Commercial azo dyes are mostly sodium salts of sulfonic acids; a few are salts of carboxylic acids. The number of sulfonic groups necessary for obtaining the requisite solubility depends largely on the molecular weight, the larger molecules usually requiring two or more sulfonic groups. The solubility and the colloidal character of the solution, and therefore the dyeing properties, are affected not merely by the number of sulfonic groups, but also by their position.

A single azo group is adequate for the production of useful dyes for wool and silk. The presence of hydroxyl, amino and carboxyl groups in the *o*- and *o*′-positions to an azo group imparts mordant dyeing properties. Azo dyes derived from salicylic acid are also mordant colors for wool and silk, and on cotton they can be applied by printing processes. The metallization may be carried out in substance or on the fiber, the suitability of a dye for a particular method of metallization being dependent on its constitution.

Considerable attention has been devoted in the research laboratories of the dye manufacturers to modifications in the constitution of azo dyes leading to brighter shades with improved leveling and fastness properties.[156a]

Azo dyes for wool. The simpler dyes are usually more level dyeing on wool than the complex, high molecular dyes. The relation between the constitution of azo dyes and their level dyeing character has not been submitted so far to extensive investigation. In the older literature empirical observations have occasionally been recorded;[157] e.g., coupling chromotropic acid with various diazotized bases, *p*-nitroaniline and cresidine yield unlevel dyes, while the dyes from aniline, *p*-aminoacetanilide and *p*-aminodimethylaniline are level dyeing. The sulfonic groups should be distributed over the entire molecule as uniformly as possible. Among simple monoazo dyes for instance, the dye (naphthionic acid ⟶ NW-acid) is more level dyeing than the dye (α-naphthylaminedisulfonic acid ⟶ β-naphthol). Speakman and Clegg[158] have found that leveling properties are mainly determined by the colloidal character of the dyes in solution, which is favored by increasing molecular weight and decreasing degree of sulfonation. For the minimum degree of aggregation and the best leveling, the sulfonic groups should be as far removed as possible from the azo group and from each other. Among the monoazo dyes from H-acid and its derivatives as second components, the leveling power decreases in the order *N*-acetyl > H-acid > *N*-*p*-toluenesulfonyl > *N*-benzoyl. In the highly sulfonated dyes which are insensitive to aggregation by acid and salt, leveling properties are determined by chemical affinity and decrease with increasing degree of sulfonation.

[156a] See also Knight, *J. Soc. Dyers Colourists* **66**, 34; 410 (1950).

[157] Schedler, *J. Soc. Chem. Ind.* **44**, 392T (1925).

[158] *J. Soc. Dyers Colourists* **50**, 348 (1934); see also Lemin and Rattee, *ibid.* **65**, 217 (1949).

The number of sulfonic groups in a dye molecule has a marked effect on the applicability of the dye to nylon.

It has been mentioned earlier that some azophenols are sensitive to alkali, and some azo dyes with free amino groups change in color with acid. The fastness of azophenols may be improved by etherification or esterification; the *p*-toluenesulfonyl group (present for instance in the fast-to-milling Polar colors) is particularly useful for the latter purpose. Further, *o*-hydroxyazo dyes exhibit much greater stability towards alkali than *p*-hydroxyazo dyes, the protecting influence in the *o*-hydroxy compounds being chelation between the hydroxyl and the azo group.

Azo dyes derived from β-naphthylamine as second component are less sensitive to acids than similar α-naphthylamine and aniline dyes; and 1-azo-2-naphthylamine and 2-azo-1-naphthylamine dyes (in which as with *o*-hydroxyazo dyes chelation between the amino and azo groups is to be expected) are much less sensitive to acid than the 4-azo-1-naphthylamine dyes. Aminonaphthols yield dyes which are much faster to acid than the naphthylamine dyes. Dyes containing secondary amino groups (e.g., Orange IV: sulfanilic acid——→diphenylamine) may also be sensitive to acid, and in this case the fastness to acid is improved by nitration, which increases the acidity of the imino group.

In contrast to level dyeing properties which are often to be found in the simplest azo dyes, the more complex disazo and trisazo dyes generally exhibit better fastness to washing. However, dyes containing more than two azo groups are of limited use because the shades tend to be unlevel, dull, and unattractive. In addition to the multiplication of azo groups, especially in the 1,4-positions, there are certain constitutional features that are favorable to the fastness of wool dyes. The *m*-disubstituted benzidines, such as benzidine-*m*-disulfonic acid, which are generally valueless for the production of substantive cotton dyes, yield (with pyrazolone and naphtholsulfonic acid coupling components) yellow to red disazo acid dyes for wool which have excellent washing fastness. Increasing the molecular weight in mono- and disazo dyes is generally an advantage, and the appended citations provide examples of the specific groups which are of especial value for this purpose. While ether groups such as methoxyl and ethoxyl are commonly present in azo dyes, more complex ethers, such as benzyl, phenyl, cresyl, and cyclohexyl, have been suggested.[159]

The general objective of producing bright atttactive shades with high all-round fastness, together with level-dyeing character, appears to be readily attained in monoazo dyes by *N*-acylation of either or both components. *N*-Acyl derivatives of aminonaphtholsulfonic acids are frequently mentioned in patents as useful second components and there are examples of commercial dyes, e.g., from *N*-acetyl-, benzoyl-, and *p*-toluenesulfonyl H-acid. Among diazonium components several patents relate to the use of amines of the type (I) in which R^1 is an alkyl group of C_1 to C_{12} or a cycloalkyl or aralkyl group; and R^2 methyl or phenyl.[160]

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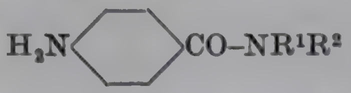
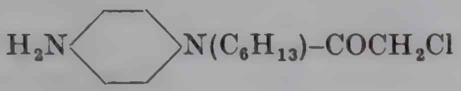
[159] IG, BP 483,442; 493,406; Ciba, BP 614,191.

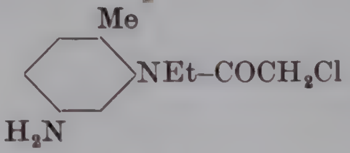


(I)

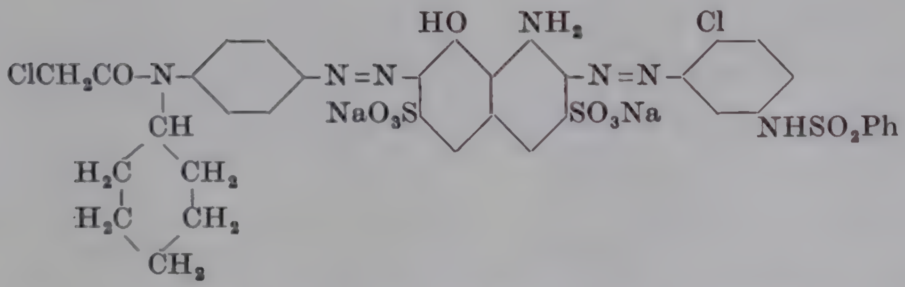
ICI claim[161] that wool dyes of very good fastness to severe washing and good light fastness are obtained by using as diazonium components *m*- or *p*-aminoacylanilides, in which the acyl group (C_{1-3}) contains a halogen atom; the acylamido group may be further substituted by an alkyl or cycloalkyl group (not more than C_6). Examples of such amines are (II) and (III). Bluish black disazo dyes of outstanding fastness, such as (IV),

(II)





(III)



(IV)

are prepared by coupling H-acid with a diazotized amine containing an *N*-benzenesulfonyl group and a diazotized halogenoacyl-*m*- or *p*-phenylenediamine.

4-Alkyl-l-naphthols give chromable azo dyes; using suitable diazonium components, the blue to blue-grey shades have good wet- and light-fastness.[161a]

Acid and acid-mordant colors containing higher alkyl groups (C_8–C_{20}) have been repeatedly mentioned in patents and the introduction of heavy alkyl groups attached to carbon, nitrogen, oxygen, or sulfur is perhaps the widest general method suggested in recent years for improving the fastness of acid dyes to severe wet treatments. Monoazo dyes in which the diazonium component is an alkyl ($>C_7$) ether of an aminophenol are claimed to possess superior fastness to milling and better exhaustion properties than corresponding dyes from the lower alkyl ethers.[162] Fastness to severe washing and milling is claimed for the monoazo dyes from diazotized amines $NH_2–C_6H_4–CO–NXY$, where X is an alkyl having C_{10-20}, preferably C_{10-16}, and Y is an aryl of the benzene series which may be further substituted by halogen, alkyl, or alkoxy groups. The second component, which is a naphthol di- or trisulfonic acid, *N*-acyl-H-acid, or a sulfoarylpyrazolone, is free from paraffin chain groups. An example is the red dye (V).[163] High washing and milling fastness in yellow to brown disazo dyes

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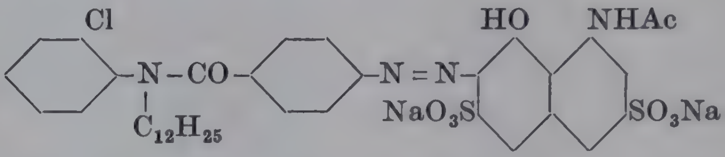
[160] E.g. Kuhlmann, BP 495,662; ICI, BP 475,423; IG, BP 469,537; 472,171; Sandoz, BP 487,621.

[161] BP 545,806; 544,409; 554,201; 554,978; 554,600–1; Knight, Stephen and ICI, BP 555,337; 556,358; 557,100; 557,842; 558,058; 569,770–1; 570,972.

[161a] Ciba, SP 245,901–3; BP 606,731. See also Geigy, BP 609,039.

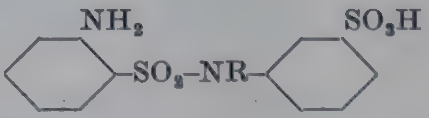


(V)

$(E^1 \leftarrow D \rightarrow E^2)$ are obtained[164] by using, as the tetrazotized diamine, diaminobenz-*N*-alkylanilides (H_2N–arylene–NR–CO–arylene–NH_2) in which R is an alkyl not less than C_{10} or a benzyl group.[165]

Phenolic ketones, $HO–C_6H_4–CO–R$, in which R is an alkyl of C_{8-15}, coupled with diazotized arylaminesulfonic acids, yield acid colors which are fast to fulling and perspiration. From similar derivatives of resorcinol, fast mono- and disazo dyes are obtainable; and as usual, if *o*-aminophenol derivatives are used as diazonium components, the dyes are chrome colors.[166]

The *p*-toluenesulfonyl group is a favorable factor for improving fastness both to light and washing and in many cases for obtaining purer shades. Examples of monoazo acid colors of this type in the commercial range are quoted later.[167] The arylsulfonyl group may be in the second component, as in *N*-*p*-toluenesulfonyl-H-acid, or it may be introduced into the diazonium component, and such amines may have the general form (VI), or may comprise similar sulfones instead of the sulfonamides.[168] The blue and blue-black disazo dyes obtained by the procedure (aminoarylsulfone—→α-naphthylamine—→1-alkyl- or arylaminonaphthalene-8-sulfonic acid) have good fastness to milling, salt water, and light.[169] Disazo dyes from tetrazo-



(VI)

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[162] Geigy, BP 511,114.

[163] Cliffe, Knight and ICI, BP 496,229.

[164] ICI, BP 475,938.

[165] ICI, BP 501,131.

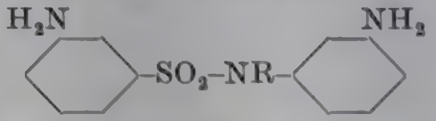
[166] Rossander and Woodward, USP 2,174,998; Desai and Joshi, IP 27,771.

[167] See also Ciba, BP 554,304–5.

[168] Geigy, BP 549,709.

[169] Geigy, BP 546,595.

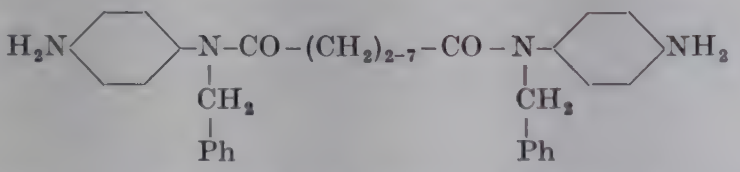
tized (VII), in which either or both the benzene nuclei may carry substituents including a short chain alkyl, and where R is an aralkyl or alkyl



(VII)

not larger than C_4, have good fastness to milling.[170] Good leveling, fastness to light and salt water are obtained in monoazo dyes in which a diazotized amine, containing a *p*-halogeno-alkyl or -alkoxytolyl sulfone group, is coupled with aminonaphthol or pyrazolone sulfonic acids; the amines are obtained by condensing a substituted benzyl chloride with arylsulfinic acid, nitrating and reducing.[171] Sulfonamide groups (e.g., SO_2NEt_2) in which the nitrogen carries alkyl substituents figure in many patents describing azo dyes which level well and have improved fastness properties. The attachment of an alkyl sulfone ($-SO_2R$) group or a dialkyl sulfonamide ($-SO_2NR_2$) group to a carbon atom in an aromatic amine used as a diazonium component for azo dyes is a common method for improving dyeing and fastness properties.[172] Diazonium salts containing acylsulfonamide groups ($-SO_2NHCOR$) in which the acyl residue is a saturated or unsaturated fatty acid ($>10C$) give with pyrazolones pure yellow dyes with excellent fastness to light, fulling, and perspiration.[173]

Diamines of the type of (VIII) yield yellow to bluish red disazo dyes of good fastness.[174]



(VIII)

The trifluoromethyl group gives improved fastness to the red azo dyes obtained by coupling diazotized 2-amino-1-aryloxy-5-trifluoromethylbenzene with NW-acid.[175]

Fastness to light is continually assuming greater importance, but our knowledge of the relation between the constitution of azo (and other groups of) dyes and their light fastness is even more empirical than in the case of wet treatments (see, however, Chapter XL).

Kienle, Stearns, and Van der Meulen[176] have attempted to correlate the structure of certain monoazo dyes with their fastness to light. The dyes used had R-salt as second component, the diazonium component being aniline or a derivative of aniline containing the substituents OH, OMe, Ph, Me, Cl, COOH, SO_3H, and NO_2 in the *o*-, *m*- and *p*-positions. Dyes of a high degree of purity were used, and were faded in water solution, on wool, and in gelatin. It was found that the solution fading was random, but the wool and gelatin fading quite reproducible. The fading of dyes in solution was very slow for a period of time, after which the fading was very rapid. This suggested an induction period followed by a different reaction mechanism and made it impossible to calculate reaction rates. Graphical representations of results of fading of wool and gelatin dyeings gave curves which fell between the curves for a first- and second-order reaction. On the assumption that the fading was a first-order reaction the reaction rates were calculated for wool and gelatin. The position *o*- to the azo group was the most sensitive to the effect of a substituent. The smallest reaction rate (fast to light) was found for the *o*-carboxy dye. Large reaction rates (fugitive) were found for the *o*-chloro and *o*-nitro dyes. The reaction rates of the *m*- and *p*-substituted dyes were analyzed by the method of Hammett[177] and were found to follow the usual linear relationship with the substituent constants. The reaction constant (Hammett's) was found to be 0.18 for dyes on wool and 0.22 for dyes in gelatin. Values less than unity, such as these, indicate that the substituent is a less important factor in fading than is the substituent in the ionization of derivatives of benzoic acid.

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[170] Cliffe and ICI, BP 502,420.

[171] Kuhlmann, BP 512,088.

[172] E.g. IG, BP 504,504.

[173] Sandoz, BP 597,131.

[174] ICI, BP 523,035.

[175] Kuhlmann, BP 540,597.

[176] *J. Phys. Chem.* **50**, 363 (1946).

The simpler azo dyes sometimes exhibit higher light fastness than complex, high molecular dyes containing two or more azo groups.[157] Many monoazo yellows, oranges, and reds derived from simple diazonium salts coupled with the pyrazolones and the naphthols possess excellent light fastness. Among such monoazo dyes with high light fastness might be mentioned Ponceau 2R (*m*-xylidine ⟶ R-acid), Tartrazine, Xylene Fast Yellow 2G (sulfanilic acid ⟶ a 5-pyrazolone), Guinea Fast Red (*p*-aminoacetanilide-*m*-sulfonic acid $\xrightarrow{\text{acid}}$ γ-acid), Azogeranine 2G (aniline ⟶ *N*-acetyl-H-acid), Fast Acid Violet R (*p*-nitroaniline-*o*-sulfonic acid $\xrightarrow{\text{acid}}$ γ-acid). Free amino groups are as a rule unfavorable to light fastness; monoazo dyes from γ-acid (acid-coupled) as second component are an exception (see below). Among the groups and components usually favorable to light fastness are: H-acid as a diazonium component; *N*-acetyl-H-acid, γ-acid (acid-coupled)[177a] and 5-pyrazolones as second components; the arylsulfone, sulfoxide, disulfoxide, and sulfonamide groups; and the $-SO_2NR_2$ group.[178]

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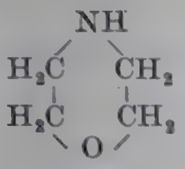
[177] Physical Organic Chemistry, McGraw Hill, New York, 1940, pp. 184–207.

[157] See p. 469.

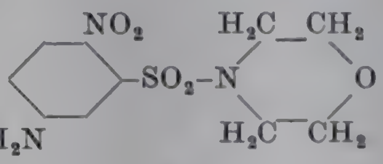
[177a] Cf. Geigy, SP 222,691–9.

[178] Cf. Ciba, BP 560,452; Geigy, BP 558,219; IG, BP 502,523.

Morpholine (IX) has now become a readily available commercial product, and azo dyes containing the morpholine nucleus are prepared for instance by condensing 4-chloronitrobenzene-2-sulfonyl chloride with morpholine (or thiomorpholine), followed by amination under pressure; the amine (X)



(IX)



(X)

is diazotized and coupled with an aminonaphtholsulfonic acid; the nitro group can be finally reduced and acetylated, yielding a red wool dye fast to light.[179] It is doubtful if the morpholine residue, rather than the $SO_2NR^1R^2$ group as a type, is responsible for conferring light fastness.

Azo dyes for silk. Among azo dyes of the acid and direct cotton classes, those which are applicable from a neutral bath with the addition of Glauber's salt are suitable, especially for tin-weighted silk, where it is necessary to avoid an acid bath.[180] The soluble chromium complexes are useful for dyeings with high fastness.

Azo dyes for leather. Brown and black are the two outstanding shades for leather, and structurally, leather dyes are mainly disazo, trisazo and tetrakisazo dyes in which *m*-phenylenediamine, resorcinol, α-naphthol and H-acid are used as end components. In view of the intrinsic difficulties in obtaining level dyeings on leather because of variations in texture and lack of affinity (particularly of vegetable tanned leather) in comparison with the textile fibers, single dyes are preferred to mixtures. Old examples of leather dyes are Bismarck Brown, Resorcin Dark Brown (naphthionic acid ⟶ resorcinol ⟵ naphthionic acid), Fast Brown G (sulfanilic acid ⟶ α-naphthol ⟵ sulfanilic acid) and Direct Deep Black EW extra (*m*-phenylenediamine ⟵ benzidine ⟶ H-acid ⟵ aniline). Tetrakisazo dyes of the pattern (sulfanilic acid $\xrightarrow{\text{acid}}$ H-acid $\xleftarrow{\text{alk.}}$ benzidine ⟶ *m*-phenylenediamine ⟵ sulfanilic acid) are black dyes for leather, which have good penetration and light fastness and are free from bronzing tendency.[181] Hexakisazo dyes prepared according to the scheme [(Ar–NH_2 $\xrightarrow{\text{acid}}$ H-acid $\xleftarrow{\text{alk.}}$ benzidine$)_2$ $\rightrightarrows$ *m*-phenylenediamine or resorcinol] are also black dyes for leather. Chromium complexes are suitable for leather dyeing. Alkylsulfonic groups are present in one of the components for some leather dyes, and apparently their function is to improve penetration. Examples are aminobenzylsulfonic acid as a diazonium component, and 1-sulfoethylamino-7-naphthol as a second component.[182] The ω-sulfonic acid may be obtained by using taurine as an intermediate in the preparation of either component.[183] Esters of sulfuric acid (e.g., 2,4-diaminophenoxyalkyl sulfuric ester) have also been suggested.[184]

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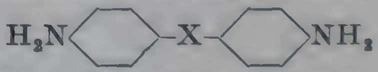
[179] West and American Cyanamid, USP 2,251,813.

[180] Tomlinson, *J. Soc. Dyers Colourists* **52**, 373 (1936).

[181] ICI, BP 543,712.

Acid colors on cotton. The acid colors are inapplicable to cellulose by a direct dyeing process. One method of imparting acid color affinity to cellulose is to convert it into a nitrogenous derivative, and there are numerous patents on the interaction of cellulose with ethyleneimine, cyanuric chloride, alkyl isocyanates, etc. These have interest as finishing treatments for cotton and viscose in order to produce waterproof, creaseproof and other special effects, but they do not appear to have found technical application with the object of dyeing the cellulose fibers with acid colors. More recently, however, there appears to be a revival of interest in printing cotton and viscose materials with acid colors and the soluble coordination complexes of the acid-mordant colors. In the " Intensifier Ciba-formaldehyde printing process ", acid and Neolan colors are printed on cotton, using a paste containing " Intensifier Ciba " (urea) and monoammonium phosphate or ammonium sulfate as a " catalyst." After printing, the fabric is steamed in presence of formaldehyde. Apparently the fixation of the acid dye to cellulose is effected by the intervention of a urea-formaldehyde resin.

Direct cotton dyes. Most of the direct cotton colors belong to one of the two main types (*a*) dyes derived from tetrazotized benzidine and analogous 4,4′-diamines, and (*b*) polyazo dyes in which J-acid or one of its *N*-substituted derivatives is an end component. With Rosophenine 10B (primuline——→NW-acid) as practically the only exception, the commercial azo dyes are of the disazo and polyazo class.

The diamines which lead to cotton affinity are listed later (Chapter XII), together with closely related diamines which do not possess this property. Briefly, the diamines producing substantive dyes are benzidine and its 3,3′-substituted derivatives; diamines of the constitution  in which X is –CH=CH–, –NH–CO–NH– or one of a few other groups; and symmetrical diamines from more complex aromatic ring systems such as carbazole and dibenzofuran. For the technically important dyes, the three outstanding diamines of the benzidine type are benzidine itself, *o*-tolidine and *o*-dianisidine. Two other parent diamines of value for the preparation of direct cotton dyes are 4,4′-diaminostilbene and 4,4′-diaminodiphenylurea.

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[182] IG, BP 493,770; 493,464.

[183] IG, BP 482,342.

[184] Geigy, BP 500,415.

While J-acid is outstanding in its ability to produce cotton affinity, other aminonaphtholsulfonic acids, such as γ-, S- and H-acids, possess this property in minor degree. Resorcinol and *m*-phenylenediamine as end components also appear to favor substantivity in polyazo dyes. Among other groups and nuclei which favor cotton affinity are the amide (–CO–NH–) group; conjugated ethylenic linkages; additional azo groups in the 1,4-positions; the benzothiazole and triazine ring systems.

The older direct cotton dyes of the benzidine class, such as Congo Red and Benzopurpurine, are still extensively employed because of their cheapness and their suitability for the many purposes that do not require good fastness to washing and to light. As a class, the benzidine dyes have a fastness to light of only 1–2 on the 1–8 scale, a few dyes such as Chrysamine G employing salicylic acid or γ-acid (acid-coupled) as end components being exceptions. J-acid dyes of the type (A⟶M⟶J-acid) are bright and level dyeing, and have good light fastness (4–5). Trisazo dyes with the azo groups in *p*-positions prepared by the scheme ($A \longrightarrow M^1 \longrightarrow M^2 \longrightarrow$J-acid) include blue and green dyes of good fastness, especially to light (4–5). The grey and black dyes in which γ-acid is an end component also possess good light fastness. Some of the yellow, orange, and brown dyes of the stilbene class have very good light fastness (5–6), together with moderate fastness to washing and chlorine. Fastness to light of 6–7, comparable therefore to the light fastness of the azoic and anthraquinone vat dyes, has been obtained in a few copper coordination complexes of direct cotton dyes containing *o,o′*-dihydroxyazo or *o*-hydroxy-*o′*-carboxyazo groups; these can be prepared in substance and applied by the usual direct dyeing process. Fastness to light and washing is claimed for the azoic dyes obtained by using diazonium salts containing a sulfonyl fluoride group;[185] and it will be of interest to examine the influence of this group on the fastness of soluble dyes.

There is a limit to the improvement in fastness, particularly to washing, which can be effected by modifications in the constitution of the dyes. It is obvious that the direct application of a soluble dye cannot lead to more than moderate fastness to washing. Direct dyeings can however be considerably improved in fastness by submitting the dyed material to further treatment. These methods of aftertreatment are discussed in Chapter XVII. The two objectives are improvements in (*a*) light fastness and (*b*) washing fastness; it is usually difficult to achieve both simultaneously, and sometimes an improvement in (*b*) is prejudicial to (*a*). The main method for improving light fastness is treatment with a copper salt. For improving washing fastness, there are several procedures available, the principle of all of them being to render the soluble dye less soluble or insoluble after application to the fiber. Treatment with formaldehyde, diazotization and development by coupling with a suitable end component, and development with a diazonium salt are three such methods.

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[185] Lecher, Parker, Hofmann and American Cyanamid, USP 2,436,697; 2,437,644.

The direct cotton dyes are of general utility for dyeing viscose, and are more widely used for this purpose than any other class of dyes. The main advantage is the simplicity and brief duration of the dyeing process, enabling the delicate material to be submitted to minimum handling. The main defect is the danger of uneven results, but the problem has now been largely solved by attacks in two directions. Viscose yarn of much more uniform quality and dyeing affinity than the early varieties is now available, and tests have been developed by which the even-dyeing characteristic of a dye can be determined.[186] The even-dyeing property is related to the capillary rise of the dye in aqueous solution on viscose thread; each dye can then be characterized by a " suction number " which defines its even-dyeing property. Thus Chrysophenine G (suction No. 19) is even dyeing, and Sky Blue FF (9) is uneven dyeing. It has been noticed incidentally that blues are generally more uneven dyeing than yellows, although even-dyeing dyes of all shades are now available. The mechanism of dyeing viscose with the direct cotton dyes is a process of diffusion in which an ultimate equilibrium between cellulose and dyebath is attained, and the even-dyeing property of a dye depends on the rapid attainment of this equilibrium. The time required for attaining equilibrium is measured in terms of the " time of half-dyeing," which varies widely from dye to dye;[187] it is 0.07 minute for Chlorazol Fast Orange GS and 155.5 minutes for Chlorazol Fast Orange AG; other examples of dyes with a small time of half-dyeing and which are therefore even-dyeing are: Chrysophenine G (0.26), Chlorazol Yellow 8GS (0.33), Diazo Brilliant Scarlet BA (0.74), Diazo Sky Blue 3GL (0.29), Diphenyl Fast Green 5GL (2.4) and Chlorazol Fast Black BKS (0.30); and examples of dyes with a large time of half-dyeing and which are uneven dyeing are: Benzoform Yellow GL (44.7), Solar Orange RGL (48.1), Benzopurpurine 10B (27.7), Sky Blue FF (15.9), Direct Green 2G (20.0), and Chlorazol Black GFS (43.8).

The Icyl dyes (ICI), which include orange, red, violet, blue, brown and blue-black dyes, are azo dyes for viscose; many members of the range are new compounds in which even-dyeing properties are obtained by using γ-acid, 1-amino-5-naphthol-7-sulfonic acid (M-acid), 1-amino-8-naphthol-4-sulfonic acid (S-acid), or their *N*-substituted derivatives, in place of J-acid as the end component in secondary disazo dyes (A⟶M⟶E), or by coupling tetrazotized 2- or 2,2′-substituted benzidines, 4,4′-diaminodiphenylamine, 4,4′-diaminodiphenyl sulfide, etc., with two moles of similar coupling components.[188]

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[186] For a general account of rayon dyeing and for references to literature, see Whittaker and Wilcock, Dyeing with Coal Tar Dyestuffs, 5th ed., Bailliere, Tindall and Cox, London, 1949.

[187] Boulton and Reading, *J. Soc. Dyers Colourists* **50**, 381 (1934); **54**, 268 (1938).

A few direct cotton dyes are suitable for wool and silk, especially the latter, producing shades fast to washing, milling and light; the light fastness is better than that of the same dyes applied to cotton. Chrysophenine G, Sirius Supra Yellow (stilbene-azo dyes), Benzopurpurine 4B, Congo Red, Deltapurpurine 5B, Diamine Fast Red F, Benzo Blue RW and Diamine Green G (benzidine dyes) and Benzo Fast Orange S (a carbonyl-J-acid dye), are examples of direct cotton dyes used in wool dyeing. On account of the sensitivity of some of these dyes to mineral acid, the dyeing is carried out from a neutral Glauber's salt bath, acetic acid being used if necessary for exhaustion.

Miscellaneous azo dyes. Water-soluble bisulfite compounds of *o*-hydroxyazo dyes containing carbonyl groups,[189] and resinous dyes which are fast to diffusion and are prepared by the action of formaldehyde on certain azo dyes, have found use in color photography.[190]

4-Vinyloxyazobenzene, prepared by heating the sodium derivative of 4-hydroxyazobenzene with vinyl chloride, can be converted into a deeply colored polymer and can be copolymerized with styrene.[191] Macromolecular azo compounds useful as ion-exchange substances, pigments or pH indicators can be prepared from diazotized or tetrazotized polymerized aminostyrenes and suitable coupling components.[192] Aminoarylguanamines can be diazotized and coupled to yield azo dyes which are capable of forming colored resins in which the color is a part of the resin molecule.[193]

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[188] Rowe, The Development of The Chemistry of Commercial Dyes, Institute of Chemistry, London, 1938, p. 26.

[189] Gáspár, BP 529,117.

[190] Eastman Kodak, BP 539,703.

[191] Penn, *India-Rubber J.* **110**, 501, 537 (1946).

[192] Skogseid, NP 73,344; see also Kenyon, Minsk, Waugh and Eastman Kodak, USP 2,274,551; Collins, BP 545,529; 546,631; Norsk Hydroelektrisk Kvaelstof A.-S., BP 622,935.

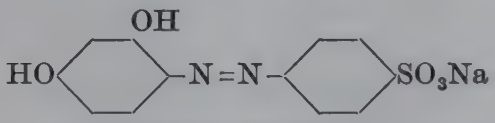
[193] Thurston and American Cyanamid, USP 2,447,440.

CHAPTER XII

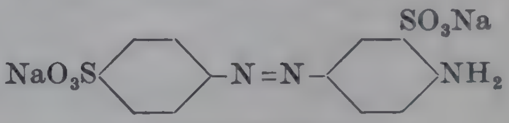
MONOAZO AND DISAZO DYES[1-6]

MONOAZO DYES

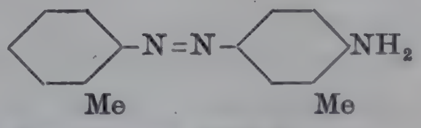
Benzene derivatives. Few among the azobenzene derivatives have survived. Cheapness being the point in their favor, the survivals include some dyes prepared in bulk for coloring materials which are consumed on a large scale (e.g., edible and other oils, foodstuffs, paper); the color in these cases is only required temporarily, or the colored product is not exposed to severe fading conditions. The diazonium component is aniline, metanilic acid or sulfanilic acid. The second components are mainly aniline and its *N*-substituted derivatives. Resorcin Yellow (Griess, 1875; CI 148), a silk and leather dye, is an example in which resorcinol is used. Aminoazobenzene is not a dye, but a useful intermediate (e.g., for Indulines).



Resorcin Yellow



Acid Yellow



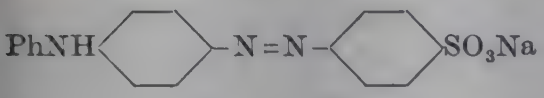
Fast Garnet GBC Base

Sulfonation yields a mixture of mono- and disulfonic acids, the sodium salt of which is marketed as Acid Yellow (Koehler, 1877; CI 16). It is a level-dyeing acid dye for wool with good fastness to light, considering its simple structure; it is also used as a food color. *o*-Aminoazotoluene (*o*-toluidine →*o*-toluidine) is used in azoic dyeing under the name of Fast Garnet GBC Base. Good yields of such aminoazobenzene derivatives can be obtained by coupling the diazonium salt with the formaldehyde-bisulfite derivative of the second component ($ArNHCH_2SO_3Na$), followed by hydrolysis of the sulfomethyl group. The diacetyl derivative of aminoazotoluene (Dimazon; Pellidol) has found use as a therapeutic agent for stimulating the growth of epithelial cells. Oil Yellow (Witt, 1876; CI 19) (aniline→

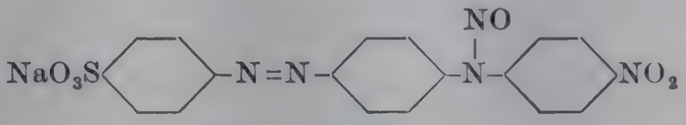
[1-6] The constitution and manufacturing details of a large number of azo dyes are described in (1) *BIOS* **961**; (2) *BIOS* **1548**; (3) *BIOS* Misc. Report **20**; (4) Report 19, Textile Series, Office of the Quartermaster General, U.S. Dept. of Commerce; (5) *Bibliography of Scientific and Industrial Reports, U.S. Dept. of Commerce,* **7** (1947); (6) Microfilm FD 2537/46.

dimethylaniline) is used for coloring oils. Methyl Orange (Griess, 1875; CI 142) (sulfanilic acid⟶dimethylaniline) and Methyl Red (Rupp and Loose, 1908; CI 211) (anthranilic acid⟶dimethylaniline) are acid-base indicators.[7]

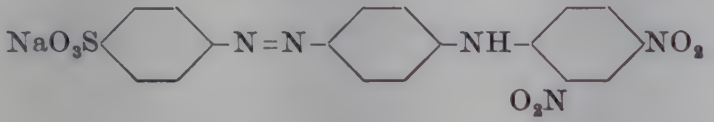
Orange IV (Witt, 1876; CI 143) (sulfanilic acid⟶diphenylamine) is still used in spite of its being sensitive to acids. The fastness to acids is improved by nitrosation, nitration and denitrosation; the mixture of nitro derivatives is Indian Yellow (Knecht, 1880; CI 146) (Azoflavine, Azo Yellow). Relatively homogeneous brands of Azoflavine (IG) are prepared by controlling the conditions of nitrosation and nitration.[1] Azoflavine 3R (conc.) is the *N*-nitroso-mononitro compound, while the *N*-nitrosodinitro compound is Azo Yellow 3G. Azoflavine 3R New and Azo Yellow 3GNN are variations of the older dyes produced by removal of the nitroso group by means of sodium bisulfite. The only dye of the series with a definite constitution is Azoflavine FFN, which is prepared by condensing 4-aminoazobenzene-4′-sulfonic acid with 1-chloro-2,4-dinitrobenzene. Silk Yellow GF (IG) is the mononitro dye obtained by nitrosation, nitration and denitrosation of the dye (4-chloroaniline-3-sulfonic acid⟶diphenylamine).[1]



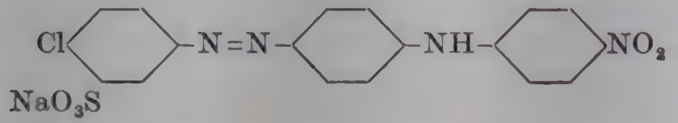
Orange IV



Azoflavine 3R



Azoflavine FFN



Silk Yellow GF

An important monoazo dye is Metanil Yellow (By; CI 138), which is a purer shade of yellow than Orange IV, less sensitive to acid, and largely used for wool dyeing, carpet printing, and coloring paper. Commercial Metanil Yellow usually contains about 3% of the isomer derived from sulfanilic acid. Diphenylamine being very feebly basic, and insoluble in water and dilute hydrochloric acid, the coupling has to be carried out with an emulsion of diphenylamine, or in alcoholic solution, or phenol or cresol solution. Details of the IG process for Metanil Yellow are as follows:[1] A solution of metanilic acid (839 kg.) and sulfanilic acid (26 kg.) is dissolved in hydrochloric acid (3200 l.) and water to make a total volume of about 8000 l. To the solution cooled to 1°, 23% sodium nitrite solution (1520 l.) is added in the course of ¾ hour, keeping the temperature at 5° by adding ice. After 2 hours stirring, more hydrochloric acid (3800 l.) is added, the temperature rising to 10°. Meanwhile diphenylamine (400 kg.) is emulsified by stirring with glue (3 kg.), Nekal A (4 kg.) and water (50 l.) at about 70°. The thick creamy mass is diluted with a solution of Nekal A (1 kg.) and water (3500 l.) at about 30°. A second batch of diphenylamine is similarly emulsified, and the whole is run into the diazonium solution in ½ hour (temperature 15–20°). After stirring for 65 hours, the mixture is diluted with water (12,000 l.) and filtered on two presses. Diphenylamine couples to 2–3% in the *o*-position, and this dye is removed by treating the press cake with soda ash (950 kg.), water (6000 l.) and sodium sulfite (100 kg.) at 50° for 1 hour. Brine (20,000 l.) is added to separate the color quickly in a readily filterable form. After 12 hours stirring at 35°, the dye is filtered and dried at 95–100° (yield 95% calculated on diphenylamine).

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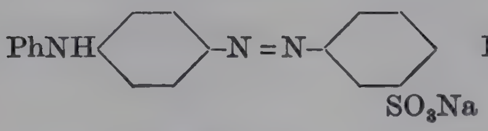
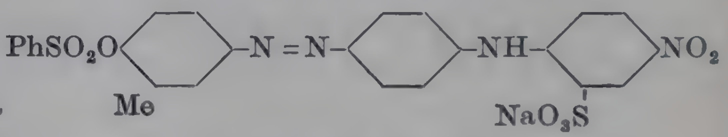
[7] For the preparation of Methyl Red, see Clarke and Kirner, *OSCV* I, p. 374.

[1] See p. 480.

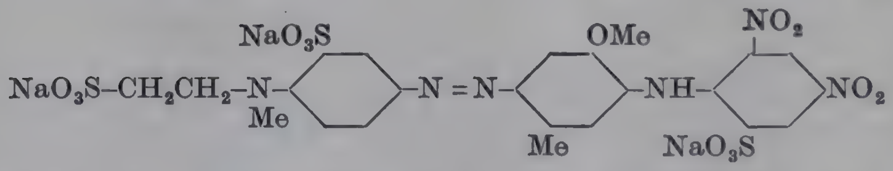
Fast Silk Yellow G (IG) is prepared by indirect diazotization of 4-nitro-4′-aminodiphenylamine-2-sulfonic acid, coupling with *o*-cresol, and esterification with benzenesulfonyl chloride.[1] An azo dye, suitable for dyeing leather, which contains a taurine residue and a dinitrodiphenylamine group, is Igenal Brown IRG (IG).[5]



Metanil Yellow

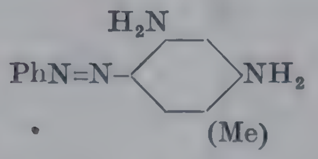


Fast Silk Yellow G

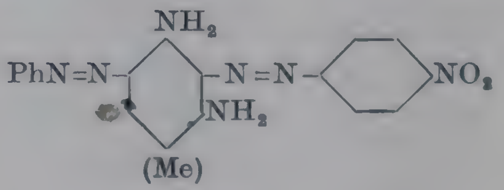


Igenal Brown IRG

Chrysoidine Y and R (CI 20 and 21), obtained by coupling benzenediazonium chloride with *m*-phenylene- and *m*-toluylenediamine are widely used basic dyes for cotton and leather. The bright brownish orange shades are fugitive; but both in dyeing and printing cotton, faster shades are obtained by developing the dyed or printed material with diazotized *p*-nitroaniline.



Chrysoidine Y (R)



Para Brown

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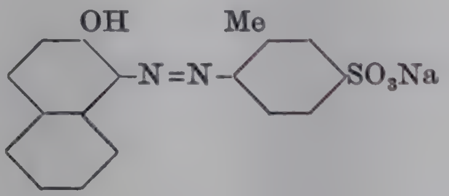
[1] See p. 480.

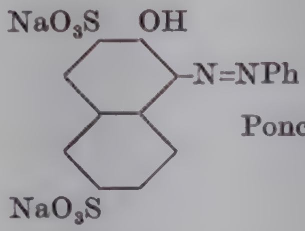
[5] See p. 480.

Naphthalene derivatives. These comprise a large group in which, while the second component is always a naphthalene derivative, the diazonium component may be a benzene or naphthalene derivative. Dyes of this type have the advantage of low cost and wide utility for ordinary purposes in which the highest all-round fastness is not required. Using benzene derivatives as first components, the shades are orange to scarlet; and if both the halves of the dye molecule are of the naphthalene series, the shades vary from scarlet to violet. With the exception of a few J-acid derivatives, they are all acid colors.

The main first components of the benzene series are aniline, *m*- and *p*-nitroaniline, *o*-anisidine and *p*-aminoacetanilide; and in the naphthalene series they are naphthionic acid, Brönner acid and H-acid. The important second components in both cases are NW-acid, G- and R-acid, H-acid, *N*-acetyl-H-acid, γ-acid and chromotropic acid. In addition, there are heterocyclic intermediates, the dyes from which are grouped separately. 1-Benzeneazo-2-naphthylamine (Oil Yellow AB) (CI 22) is a permitted food color. Orange I (Griess, 1876; CI 150) and II (CI 151) (sulfanilic acid ⟶ α- and β-naphthol respectively) are sensitive to acids, but continue to be manufactured. Orange R (Mühlhäuser, 1887; CI 161) is used extensively for dyeing wool, silk and leather, and for the manufacture of lakes. Details of the IG process for Orange II are as follows:[1] *o*-Toluidinesulfonic acid (26 kg.) and sulfanilic acid (145 kg.) are dissolved in water (6700 l.) at 23°. The solution is made weakly acid to Congo Red by the addition of hydrochloric acid (about 1400 l.), and then strongly acid (1800 l. hydrochloric acid) for diazotization. After stirring and leaving overnight, ice (5000 kg.) is added to bring the temperature to 6°, and 23% sodium nitrite solution (2100 l.) run in. The mixture is stirred for 2 hours at 8–10°, and run into a solution of β-naphthol (995 kg.), 50% caustic soda (680 kg.), soda ash (84% purity; 130 kg.) and salt (500 kg. in water 15000 l.), cooled to 8°. After half the diazonium solution has been added, 50% caustic soda (20 kg.) diluted with water (70 l.) is added and then the remaining diazonium solution. During the coupling, salt (900 kg.) is added gradually. The temperature at the end is 16° and the pH 9.1–9.4. After

Orange R





Ponceau 2G

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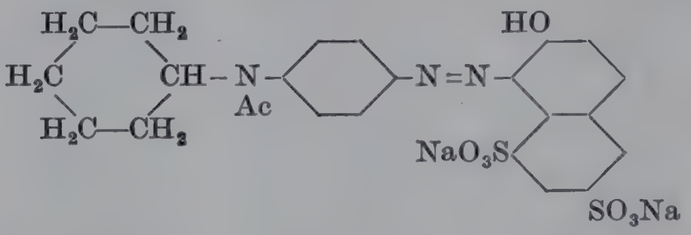
[1] See p. 480.

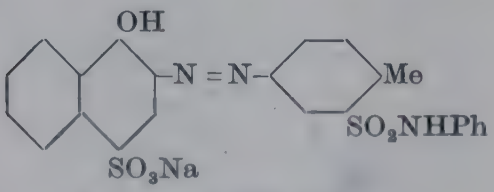
two hours stirring, hydrochloric acid is added to bring the pH to 8.2–8.5, the mixture stirred and filtered on two presses. The press cake is dissolved to form a 35–37% solution, which is then dried on a double-drum dryer.

Azo Eosine G (By; CI 114) (*o*-anisidine→NW-acid) dyes wool a bluish-red of moderate light fastness and good fastness to acid and alkali. Ponceau 4GBL (Griess, 1878; cf. CI 26) is (aniline+toluidines→Schaeffer acid).[6] Orange G or GG (MLB; CI 27) and Ponceau 2G (MLB; CI 28) (aniline→G- and R-acids) are level dyeing and have good light fastness, but poor washing fastness; comparing the two isomeric dyes between themselves, the effect of the change in the position of one of the sulfonic groups from 8 to 3 is interesting; the shade is redder, faster to washing, less level-dyeing and less fast to light. Guinea Fast Red RR (IG) (*o*-anisidine→acid GR) is a level dyeing acid color with moderate fastness to light.[2] Sorbine Red (BASF; CI 54) (*p*-aminoacetanilide→acid GR) has good fastness to light and washing. Supramine Orange G (IG) (*p*-amino-*N*-cyclohexylacetanilide→G-Acid) is a level dyeing acid color with good fastness to light (6).[2, 8] Supramine Red B (IG) (5-*N*-ethylbenzamido-*o*-toluidine→NW-acid) is level dyeing and fast to carbonizing, but has only moderate fastness to light (4) and to milling (2–3).[2] Supramine Red GG is (*p*-toluidine-2-sulfonic acid→NW-acid).[6]

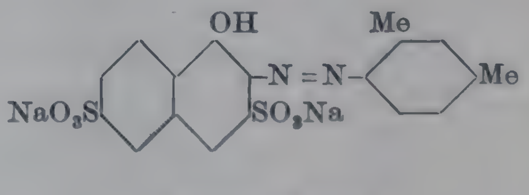


Supramine Orange G

Anthralan Orange GG (IG) (orthanilic acid→*N*-acetyl-J-acid) is a wool dye with very good light fastness.[2] Milling Orange GN (IG) and Supramine Red R (IG) are prepared by coupling diazotized *p*-toluidine-2-sulfonanilide with Schaeffer acid and NW-acid respectively;[2] they are level-dyeing dyes with good fastness to milling, these properties being usually associated with the arylsulfonamido group.



Supramine Red R



Palatine Scarlet

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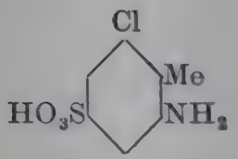
[6] See p. 480.

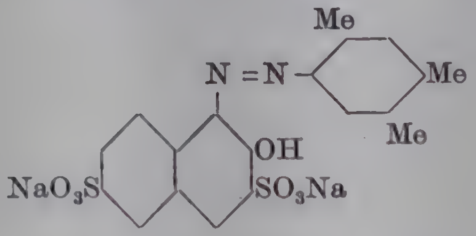
[2] See p. 480.

[8] The figures within brackets are fastness grades; see Chapter VI.

Palatine Scarlet (BASF; CI 77), introduced as a substitute for cochineal, is moderately fast to light. Cresidine⟶1-naphthol-3,7-disulfonic acid gives Brilliant Lanafuchsine SL (IG).[2] Ponceau R or 2R (MLB; CI 79) (*m*-xylidine⟶R-acid) has good fastness to light and washing, and comparing it with its aniline analog (Ponceau 2G) the influence of the *m*-dialkyl groups is noteworthy. Ponceau 3R (MLB; CI 80) is the analog from ψ-cumidine; besides being a level-dyeing bluish-scarlet dye for wool, it is a permitted food color. By coupling diazotized 6-chloro-*o*-toluidine-4-sulfonic acid (I) with a mixture of α-naphthol (92%), β-naphthol (4%) and resorcinol (4%), a useful leather dye (Acid Leather Brown EG) (IG) is obtained;[1] in addition to the three monoazo dyes, it is likely that the product contains some of the disazoresorcinol compound because of the readiness with which resorcinol couples. Coupling diazotized 4-nitroaniline-2-sulfonic acid with methyl-β-naphthylamine, the product is a violet dye, Victoria Fast Violet B extra (IG).[2] Useful brown dyes with good fastness to light and milling, dyeing wool and silk from a neutral bath, are obtained from *N*-phenyl-γ-acid alkali-coupled; examples are Supramine Brown R (IG) (4-nitro-*o*-anisidine⟶phenyl-γ-acid) and Supramine Brown G (4-*N*-ethyl-*N*-acetyl-*m*-toluylenediamine⟶*p*-anisyl-γ-acid).[6]

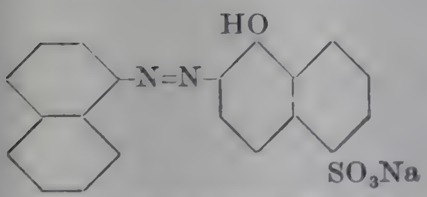
(I)



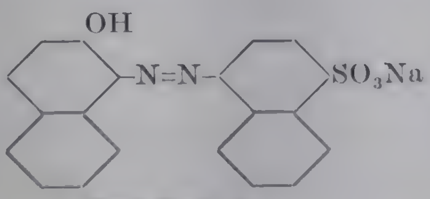


Ponceau 3R

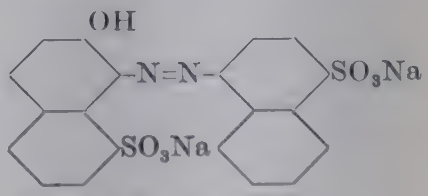
The red acid dye Double Ponceau R (By; CI 84) is fast to acid and alkali, and is useful in the preparation of lake pigments with good fastness to light. Isomeric with this is Double Ponceau 4R (IG) (1-naphthylamine-5-sulfonic acid⟶β-naphthol).[1] Fast Red A (Caro, 1877; CI 176) was the first red azo dye, and is still important on account of its cheapness and adequacy for many purposes; the IG production averaged over 65000 kg. a year. The isomer from α-naphthol (Fast Brown N or R; Naphthylamine Brown) (Caro, 1878; CI 175) is also a useful dye. Other acid dyes employing



Double Ponceau R



Fast Red A



Crocein Scarlet 3BX

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[2] See p. 480.

[1] See p. 480.

[6] See p. 480.

TABLE I

Lake	*Constitution of the azo dye*	
	Diazonium component	*Second component*
Helio Orange CAG	Aniline	Schaeffer acid
Helio Orange TD	*o*-Chloroaniline	Schaeffer acid
Helio Orange GL	2-Nitroaniline-4-sulfonic acid	R-Acid
Permanent Orange R (CI 156)	5-Chloroaniline-2-sulfonic acid	β-Naphthol
Primazine Orange G	4-Aminoazobenzene-3,4′-disulfonic acid	2,4-Dihydroxyquinoline
Pigment Scarlet 3B (CI 216)	Anthranilic acid	R-Acid
Pigment Scarlet G (CI 215)	Anthranilic acid	Schaeffer acid
Helio Red RMT	*m*-Toluidine-6-sulfonic acid	β-Naphthol
Lake Red P Pigment Lake Red LP (CI 158)	4-Nitroaniline-2-sulfonic acid	β-Naphthol
Lake Red C Lake Red Toner LCD; LCL (CI 165)	6-Chloro-*m*-toluidine-4-sulfonic acid	β-Naphthol
Lake Red D (CI 214)	Anthranilic acid	β-Naphthol
Helio Red BL	*o*- and *p*-Toluidines (92 and 8)	1-Naphthol-5-sulfonic acid
Lithol Red R; 3BN (CI 189)	Tobias acid	β-Naphthol
Lithol Red GG	6-Chloro-*p*-toluidine-3-sulfonic acid	β-Naphthol
Lithol Red 3G	3,4-Dichloroaniline-6-sulfonic acid	β-Naphthol
Permanent Red B	4-Chloroaniline-3-sulfonic acid	Hydroxynaphthoic acid
Permanent Red BB; F5R	6-Chloro-*p*-toluidine-3-sulfonic acid	Hydroxynaphthoic acid
Permanent Red 6B	*p*-Phenetidine-3-sulfonic acid	β-Naphthol
Permanent Red Toner NCR	2-Chloro-5-amino-4-sulfobenzoic acid	β-Naphthol
Lithol Rubine BN; BK Permanent Red 4B; F6R	*p*-Toluidine-3-sulfonic acid	Hydroxynaphthoic acid
Lithol Rubine GK	4-Chloroaniline-3-sulfonic acid	Hydroxynaphthoic acid
Lithol Rubine 3B	2-Naphthylamine-8-sulfonic acid	Hydroxynaphthoic acid
Astazin Red G	*p*-Chloroaniline	R-Acid
Astazin Red B	2-Chloro-*p*-toluidine	R-Acid
Pigment Carmine 3B	*m*-Tolidine	R-Acid – 85% Schaeffer acid – 15%
Helio Bordeaux BL	α-Naphthylamine	1-Naphthol-5-sulfonic acid
Helio Bordeaux 6BL	*p*-Phenetidine-2-sulfonic acid	β-Naphthol
Bordeaux Toner R Lake Bordeaux BN	Tobias acid	Hydroxynaphthoic acid
Permanent Bordeaux RN	3-Amino-4-methoxytoluene-6-sulfonic acid	Hydroxynaphthoic acid

diazotized naphthionic acid are Crocein Scarlet 3BX (By; CI 183) (⟶ crocein acid), Amaranth (Baum, 1878; CI 184) (⟶R-acid) and Cochineal Red A (Brilliant Ponceau 4R) (Baum, 1878; CI 185) (⟶G-acid). Amaranth is used for coloring foods and pharmaceutical preparations. Fast Red B (Baum, 1878; CI 88) (α-naphthylamine⟶R-acid) is a largely used bordeaux-red dye for wool and silk. Silk Red G (IG) is obtained by coupling diazotized Dahl acid (mixed 2-naphthylamine-5- and 8-sulfonic acid) with β-naphthol.[1]

The calcium and barium salts of several monoazo dyes constitute valuable lake pigments. A series of the dyes (IG) used for this purpose are listed in Table I.[1–5, 9] Lake-making is a process requiring considerable technical skill, since the properties of the lake largely depend on its physical state, which in turn is governed by various factors in the preparation, such as the pH of the coupling medium and the conditions of precipitation, filtration, washing, drying and grinding. To quote two isolated examples of methods of preparation which influence the quality of the pigment, azo lakes with uniform physical properties are obtained by diazotizing the amine in acid solution in presence of a suspension of the coupling component, then raising the pH to 7.8 to effect coupling, and converting into the barium lake.[10] It is claimed that the barium lake from the dye (2-naphthylamine-1-sulfonic acid⟶β-naphthol) is darker, cleaner, stronger and more bronzy, when the dye is prepared in the presence of a small amount of another azo dye (e.g., the dye from the same diazonium salt and phenylmethylpyrazolone) which is not capable of diazotization or coupling.[11]

Azo dyes from 2-hydroxy-3-naphthoic acid generally yield brighter and faster lakes than the corresponding β-naphthol derivatives. The calcium lake from Brilliant Lake Red R (MLB; CI 35) (aniline⟶2-hydroxy-3-naphthoic acid) is beautiful and fast to light. Coupling the same acid with diazotized 2,4-dinitroaniline-6-sulfonic acid, the dye (Hansa Rubine) (MLB; CI 160) yields bluish-red lakes; with *p*-toluidine-3-sulfonic acid, the calcium lake of the dye Permanent Red 4B extra (AGFA; CI 163) is a brilliant ruby-red with good fastness properties; with 6-chloro-*m*-toluidine-4-sulfonic acid the bright red lakes are notable for their fastness to light.

Among the Vulcan colors (IG), which are prepared for use in the rubber industry, several are barium lakes of azo dyes. Examples are Vulcanosin Red B, Red 5B and Violet BB, which are prepared from Anthosine B, 5B

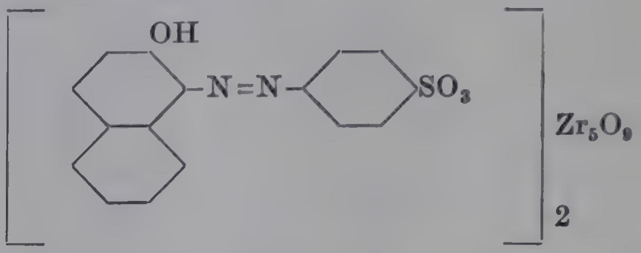
[1–5] See p. 480.

[9] *BIOS* **1661** describes the IG methods of preparation of a large number of organic pigments and lake dyestuffs.

[10] Locke, USP 2,418,416. See also USP 2,478,768.

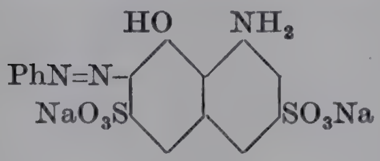
[11] du Pont, BP 517,456.

and Violet BB.[1] Zirconium chloride forms compounds (e.g., Ia) with acid dyes which have unusual tinctorial strength and have been recently introduced in the pigment industry.[11a]

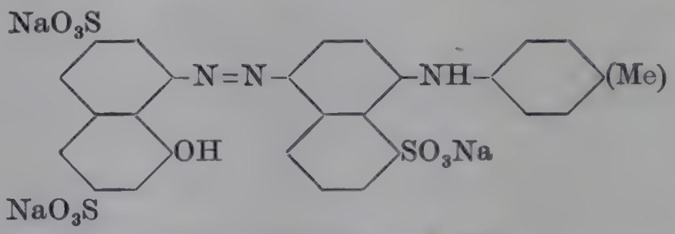


(Ia)

Alkaline coupling of H-acid leads to a series of useful monoazo dyes, such as Fast Acid Fuchsine B (By; CI 30) which has, however, poor light fastness. A further use for H-acid is as a first component; Sulphon Acid Blue R and B (By; CI 208 and 209) are largely used dyes with good fastness to light (6) and milling (3). Lanacyl Violet BF (C, CI 207) is (H-acid⟶*N*-ethyl-α-naphthylamine). An example of the use of S-acid as the diazonium component is Tolyl Blue NB (IG) (S-acid⟶phenyl-peri-acid).[6]

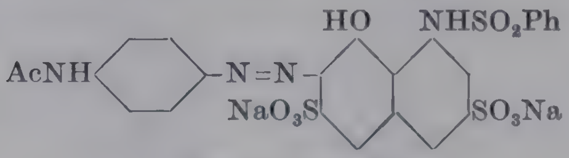


Fast Acid Fuchsine B

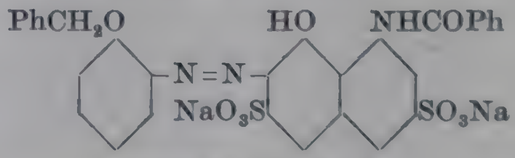


Sulphon Acid Blue R (B)

Fastness to light is improved by using *N*-acylated H-acid as the second component; in some cases there is also an increase in the fastness to wet treatments. Amido Naphthol Red G (MLB; CI 31) (aniline⟶*N*-acetyl-H-acid) (Azogeranine 2G, BDC) is fast to light (5–6) and largely used. The great increase in light fastness (contrast Fast Acid Fuchsine B and Azogeranine 2G) by what would at first sight appear to be a minor modification in structure—the acetylation of an amino group—is remarkable. Supramine Red 3B (IG) (*o*-toluidine⟶acetyl-H-acid)[2] has good fastness to light (5), but both Azogeranine 2G and Supramine Red 3B have low milling fastness (1–2). Amido Brilliant Red B is the *o*-anisidine analog.[6] Amido Naphthol



Lanafuchsin 6B



Anthosine Violet B

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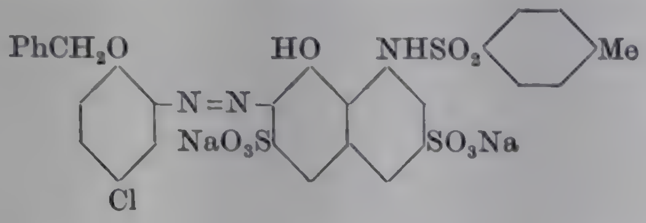
[1] See p. 480.

[11a] Blumenthal, *J. Chem. Education* **26**, 472 (1949).

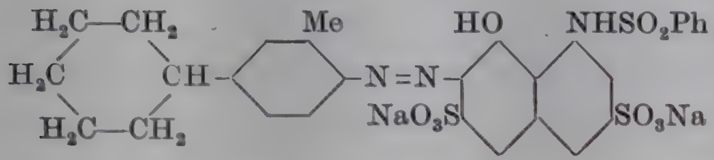
[6] See p. 480.

[2] See p. 480

Red 6B (*p*-aminoacetanilide⟶acetyl-H-acid) (MLB; CI 57) is useful for deep reds on wool. Lanafuchsin 6B (IG) (*p*-aminoacetanilde⟶*N*-benzenesulfonyl-H-acid) has excellent leveling, but inferior fastness properties.[2] Anthosine Violet B and Polar Brilliant Red 3B (Gy) are prepared from the *N*-benzoyl and the *N*-*p*-toluenesulfonyl derivatives of H-acid; Polar Brilliant Red 3B is a dye with excellent fastness to light, washing and acid.[12] Brilliant Sulphon Red B (Böniger, 1899; CI 32) is the analog of Polar Brilliant Red 3B with aniline as the first component. Supranol Brilliant Red 3B (IG) (5-cyclohexyl-*o*-toluidine⟶benzenesulfonyl-H-acid) has moderate leveling and fastness properties.[2]



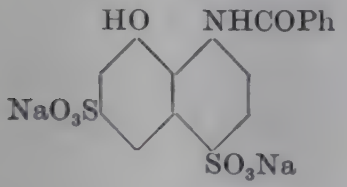
Polar Brilliant Red 3B

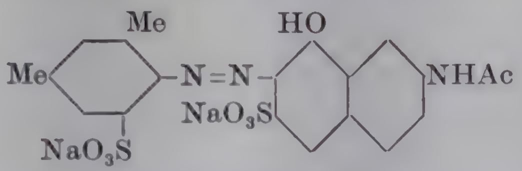


Supranol Brilliant Red 3B

A series of acid dyes of the Anthosine class (IG) are prepared[1, 2] from *N*-benzoyl-K-acid (II) and the 2,4-dichloro- and 2,5-dichlorobenzoyl analogs (III and IV). Examples are Anthosine B (BASF; 1912) (*m*-chloroaniline⟶III); 3B (*m*-toluidine⟶II); 5B (IG) (*o*-anisidine⟶III); and Violet BB (BASF; 1912) (α-naphthylamine⟶II). Supranol Brilliant Red G (IG) (4-Amino-N-cyclohexylacetanilide⟶II) has good light fastness (5–6) and moderate milling fastness (2–3).[2] Using (IV), Anthosine BN (*m*-chloroaniline⟶IV), Anthosine 5BN (*o*-anisidine⟶IV), and Supramine Brilliant Red FB (IG) (4-aminocyclohexylbenzene⟶IV), are obtained.[1, 2] *N*-Acetyl-γ-acid, coupled with diazotized *p*-amino-*N*-ethylbenzanilide and *m*-4-xylidine-5-sulfonic acid respectively, gives Supramine Red BL and GL (IG).[2] Level orange shades are obtained by coupling an aniline-*o*-sulfonic acid with 1-acylamido-6-naphthol-4-sulfonic acid.[13]

(II)





Supramine Red GL

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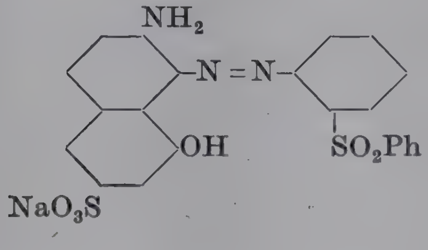
[2] See p. 480.

[12] Fierz-David, Kunstliche Organische Farbstoffe, Ergänzungsband, Springer, Berlin, 1935.

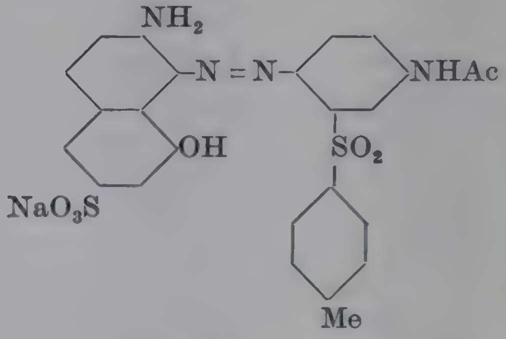
[1] See p. 480.

[13] IG, BP 502,523.

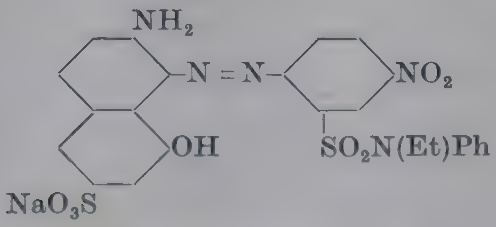
A series of useful dyes, some of which have high light fastness, are obtained by coupling various diazonium salts with γ-acid under acid conditions. The shades are red to reddish blue. Examples,[2, 14] using the indicated diazonium components, are: Guinea Fast Red (Anthralan Red G) (IG) (4-aminoacetanilide-3-sulfonic acid), Anthralan Red GG (IG) (3-aminoacetanilide-4-sulfonic acid), Supramine Red BLL (IG) (4-amino-*N*-ethylacetanilide-2-sulfonic acid), Fast Acid Violet R (*p*-nitroaniline-*o*-sulfonic acid) and Fast Acid Violet B (*p*-phenylenediamine-*o*-sulfonic acid).[14] Victoria Fast Violet RR extra (IG) (Fast Acid Violet R, By) has poor milling fastness (1–2), but good light fastness (5).[2] Anthralan Red B (IG) and Kiton Fast Red 4BL (Cb; ST 108), which are fast to washing as well as to light, involve the use of diazonium salts containing an arylsulfone group for effecting an improvement in washing fastness. In the Polar colors (Gy) of the azo and pyrazolone series fastness to milling is obtained by acylating a phenolic hydroxyl by means of *p*-toluenesulfonyl chloride. Supramine Blue R (IG) possesses only moderate fastness to milling (3) and light (4), and does not level very readily; reduction of the nitro group leads to Supramine Bordeaux B (IG), which has considerably improved fastness to light (6–7) and better leveling power. Acylation of Supramine Bordeaux B in aqueous solution by means of acetic anhydride gives Anthralan Bordeaux B (IG).[2] Sulphon Acid Blue 2R, a useful reddish blue dye with good fastness to light and washing, is (4-chloro-2-aminodiphenyl ether



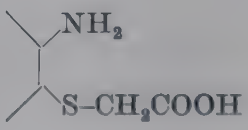
Anthralan Red B



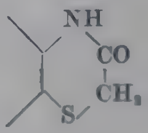
Kiton Fast Red 4BL



Supramine Blue R



(V)



(VI)

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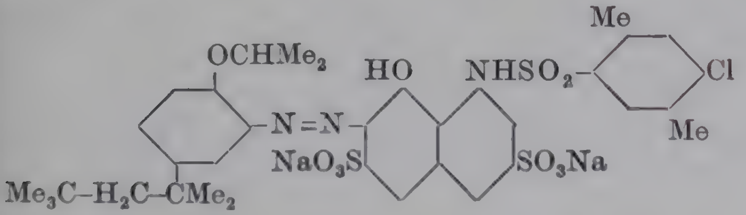
[2] See p. 480.

[14] Fierz-David, Kunstliche Organische Farbstoffe, Springer, Berlin, 1926.

4′-sulfonic acid⟶*N*-phenyl-γ-acid).[6] An interesting example of a black monoazo dye in which the diazonium component is a benzene derivative is Supramine Black BR (IG) (5-nitro-*o*-anisidine⟶phenyl-γ-acid), an acid dye with good fastness to light and milling.[2]

There have been two recent British achievements in the production of fast dyes for wool. One is that the fastness to severe wet treatments is greatly improved by the introduction of one or more alkyl groups (C_4 to C_{20}), which may be attached to a nitrogen atom in an amino or amido group, or to oxygen or sulfur as an ether, ester or thioether group, or to a carbon atom in one of the aromatic nuclei in the dye molecule.[15] Examples are Carbolan Yellow 3GS and Carbolan Crimson BS (ICI).[16] The second discovery relates to compounds which contain *o*-aminothioglycolic acid groups (V). These are water-soluble and dye wool from an ammonium acetate bath. When the dyes are treated on the fiber with hot dilute acid, cyclization takes place with the formation of the insoluble lactams (VI), which are fast to washing, milling and potting. Similar devices are also useful in the acid colors of the anthraquinone series.

Supranol Brilliant Red 6B (IG) is constituted on the Carbolan model; it is a dye with a remarkably clear shade, level dyeing character, good fastness to light, and very good fastness to other agencies.[3] Supramine Orange 3939 (IG) is (*N*-cyclohexyl-*N*-acetyl-*p*-phenylenediamine⟶*N*-β-chloropropionyl-J-acid).[5]



Supranol Brilliant Red 6B

When α-naphtholsulfonic acids in which coupling takes place *ortho* to the hydroxyl, such as NW-acid, α-naphthol-5-sulfonic acid, 1,8-dihydroxynaphthalene-4-sulfonic acid and chromotropic acid are employed as the second components, the acid dyes can be afterchromed for improving the wet fastness; oxidation to quinonoid forms apparently takes place, followed by attachment of the metallic radical to the dye-fiber complex. A characteristic of these afterchrome colors, as distinguished from the dyes which are applied to premordanted fibers or in a single bath by the metachrome process, is the profound change in color that takes place during the treatment with dichromate. Thus Carmoisine (Witt, 1883; CI 179) (naphthionic acid⟶NW-acid) and Chrome Fast Blue R (Cb; CI 180) (naphthionic acid⟶α-naphthol-5-sulfonic acid) dye wool red and bluish-red as acid colors, converted by afterchroming into violet-blue and navy blue. The alteration in shade is important from the practical angle, as well as the point of view of the constitution of the final product.[17] A dye using dioxy-S-acid is Azo Fuchsine G (By; CI 153), which is much more valued as a red acid dye, but is converted into black by afterchroming. Chromotropic acid is the intermediate for the afterchrome colors introduced originally by MLB (1890) as the Chromotropes. As acid colors they dye bluish red shades, which change to various tones of deep blue to black by afterchroming. The diazonium components for Chromotrope RR (CI 29), 2B (CI 45), 6B (CI 56), 10B (CI 90), and 7B are aniline, *p*-nitroaniline, *p*-aminoacetanilide, α-naphthylamine, and *p*-aminoazobenzene. Victoria Violet 4BS (VII; $R = NH_2$) may be prepared by the reduction of Chromotrope 2B with sodium sulfide, or by the hydrolysis of the acetyl group in Chromotrope 6B. In Azo Acid Blue B (IG), $R = NHMe$.[2] Brilliant Naphthol Blue B (IG) is (5-acetamido-*o*-toluidine⟶chromotropic acid; hydrolyze the acetyl group).[6] "Chromotropic Blue" (*p*-aminodiethylaniline⟶chromotropic acid) is a pH indicator and a reagent for metals.[18]

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[6] See p. 480.

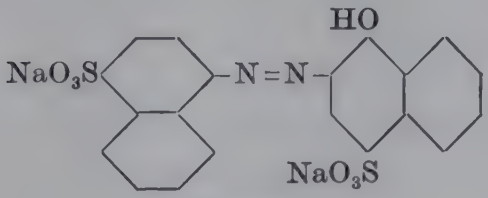
[2] See p. 480.

[15] ICI, BP 443,835; and other patents quoted in Chapter XI.

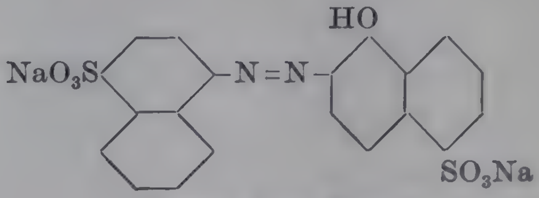
[16] At the present time " Carbolan " indicates wool dyes of a certain fastness standard, rather than a chemical type.

[3] See p. 480.

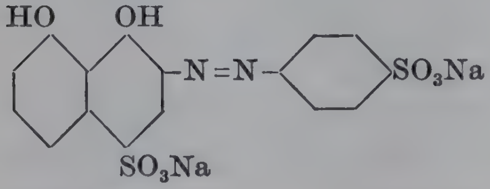
[5] See p. 480.



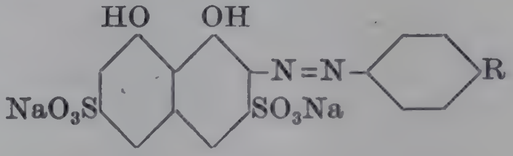
Carmoisine



Chrome Fast Blue R



Azo Fuchsine G



(VII)

Chromotrope RR; 2B; 6B
Victoria Violet 4BS
($R = H$; NO_2; NHAc; NH_2)

o-Hydroxyazo dyes derived from anthranilic acid as the first component are suitable for mordant dyeing by the afterchrome process, although they are more important in the manufacture of lakes. Acid Alizarin Red B (IG) (anthranilic acid⟶R-acid) afterchromes to a bordeaux red with good light fastness.[1] Acid Alizarin Red BT is (anthranilic acid⟶condensation product of Schaeffer acid chloride and anthranilic acid); and Acid Anthracene Brown 3G is (anthranilic acid⟶phenyl-γ-acid).[6] The dye (anthranilic acid⟶4-acetyl-1-naphthol-8-sulfonic acid), after chromation, dyes wool a wine-red from a formic acid bath.[18a] Diazotized 2-amino-3-naphthoic acid and its sulfonic acids couple with acylacetarylamides to give greenish-yellow dyes of good fastness to light, which may be afterchromed to improve milling fastness. Triazoles such as (VIIa), prepared by the sodium sulfide

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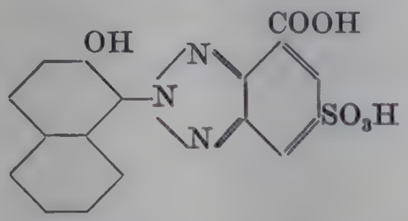
[17] See Chapters XIII and XIV.

[2] See p. 480.

[18] Steigmann, *J. Soc. Chem. Ind.* **66**, 353 (1947).

[6] See p. 480.

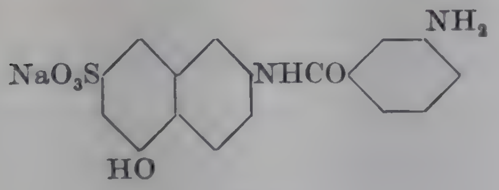
[1] See p. 480.



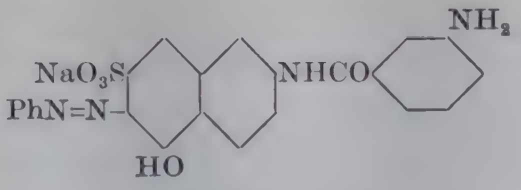
(VIIa)

or zinc-ammonia reduction of the azo dye (3-nitro-2-amino-5-sulfobenzoic acid⟶β-naphthol), have good affinity for wool, and by aftertreatment with chromium or copper salts, shades of high light fastness are obtained.[18b]

J-acid derivatives represent the only monoazo dyes which are substantive to cotton, and are therefore of interest from the point of view of the relation between the constitution of dyes and their affinity for cellulose. The simplest intermediate for this purpose is *m*-aminobenzoyl-J-acid (VIII), prepared by condensing J-acid with *m*-nitrobenzoyl chloride and reducing the product. Coupling this in alkaline solution with benzenediazonium chloride, the monoazo dye, Rosanthrene O (Cb; CI 324a), is a fugitive direct cotton dye. By diazotizing the free amino group on the fiber and



(VIII)



Rosanthrene O

coupling with alkaline β-naphthol, the orange shade is intensified and brightened, and the fastness to washing, but not to light, is improved. Using more complex diazonium salts, a series of Rosanthrene colors (Cb) were obtained. A more valuable second component than (VIII) was its *m*-aminobenzoyl derivative prepared by condensing (VIII) with *m*-nitrobenzoyl chloride and reducing the new nitro group. Diazo Brilliant Orange GR extra (CI 324) and Diazo Brilliant Scarlet BG (IG) are azo dyes from this intermediate and diazotized aniline and *o*-anisidine respectively.[2] These dyes can be diazotized on the fiber, and developed; Diazo Brilliant Orange, developed with β-naphthol, thus gives a bright orange (light fastness 2; washing fastness 2–3).[23]

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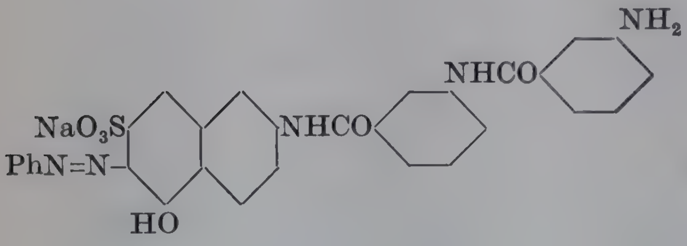
[6] See p. 480.

[18a] Geigy, SP 242,843.

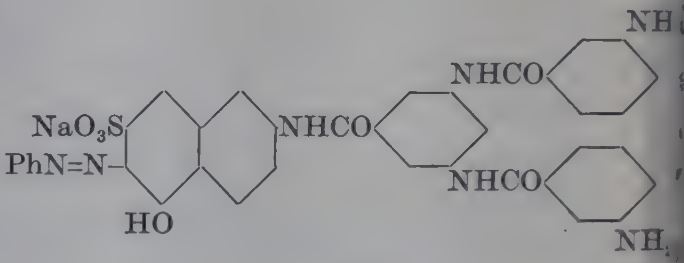
[18b] Conzetti and Schmid, USP 2,412,767.

[2] See p. 480.

There has been a revival of interest in monoazo dyes derived from J-acid, capable of diazotization and development on the fiber. An interesting dye of this type is (IX), in which 3,5-dinitrobenzoic acid is an intermediate; (IX) may be tetrazotized and developed with suitable end components.

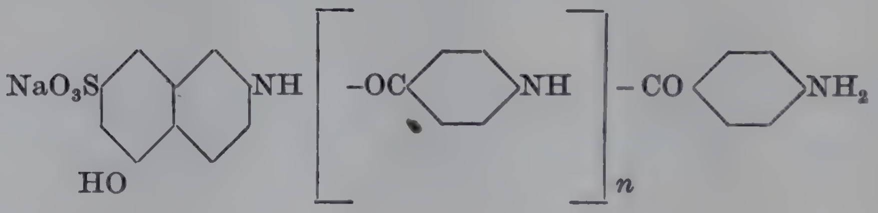


Diazo Brilliant Orange GR extra



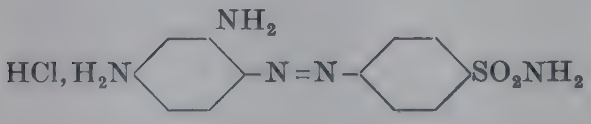
(IX)

In the azo dyes derived from *N*-acyl-J-acids of the type (X or the *m*-aminobenzoyl analog), substantivity is in the order of increasing number of amide groups.[19]

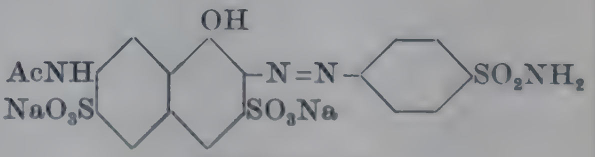


(X)

Medicinal dyes. Ethoxazene (*p*-phenetidine⟶*m*-phenylenediamine), Pyridium (aniline⟶2,6-diaminopyridine) and Neotropin (2-butoxy-5-aminopyridine⟶2,6-diaminopyridine) are interesting monoazo dyes which are useful antiseptics for genitourinary infections and are staining media for tumors. Azo dyes such as Prontosil and Neoprontosil, derived from sulfanilamide, have now been largely displaced by the parent amine, since the dyes undergo fission to a mixture of primary amines in the animal body and have no advantage over the sulfanilamides themselves. However, conversion into an azo dye is a convenient method of



Prontosil



Neoprontosil

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[23] See Chapter XVII.

[19] Voroshcov and Bibischev, *J. Applied Chem.* (*U.S.S.R.*) **11,** 1486 (1938).

imparting water-solubility to drugs with primary amino groups; thus the azo dye (stibanilic acid $\xrightarrow{\text{alk.}}$ H-acid) has been used in the treatment of trypanosomiasis (sleeping sickness).[20]

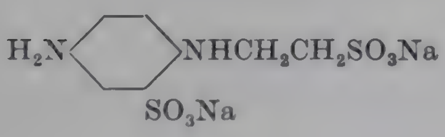
DISAZO DYES

The disazo dyes are very large in number and they can be prepared by a variety of methods. It is therefore convenient to divide them further in accordance with the nature of the diazonium and coupling components and the order in which the diazotization and coupling reactions are carried out.

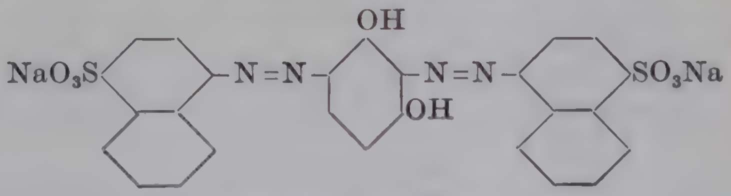
PRIMARY DISAZO DYES

The use of a single second component, with which two moles of the same diazonium salt or one mole each of two different diazonium salts are coupled, characterizes the primary disazo dyes ($A^1 \longrightarrow Z \longleftarrow A^2$). Depending on the molecular weight and the use of benzene or naphthalene derivatives, the depth of color in the series varies from brown to black. The only benzene intermediates which can be used as Z are *m*-phenylenediamine, resorcinol and some of their derivatives.

Resorcin Brown (AGFA; CI 234) (sulfanilic acid⟶resorcinol⟵*m*-4-xylidine) is a largely used leather dye. The taurine derivative (I) is useful for the preparation of leather dyes. An example is Igenal Brown IGG (IG) (I⟶resorcinol⟵4-nitroaniline-2-sulfonic acid).[4] Coupling resorcinol in the 2,4-positions with two moles of naphthionic acid, Resorcin Dark Brown (AGFA; CI 235) is an acid color for wool with moderate fastness, the fastness to washing being improved if the dyeing is carried out on chrome mordanted wool.



(I)



Resorcin Dark Brown

Cotton Brown N (IG) is (α-naphthylamine⟶*m*-phenylenediamine⟵naphthionic acid).[6] Acid Brown R (AGFA; CI 232) (aniline⟶*m*-phenylenediamine⟵naphthionic acid) is a wool dye. Fast Brown G (CI 239) (sulfanilic acid, 2 moles $\rightrightarrows$ α-naphthol) is mainly used for dyeing leather and for shading purposes in wool dyeing. A black with limited use, Palatine

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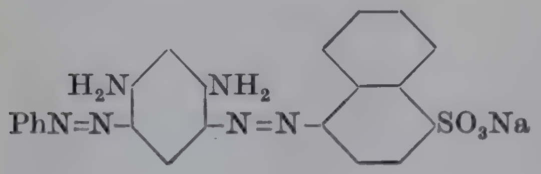
[20] Dunning and Macht, *J. Pharmacol. Exptl. Therap.* **32,** 205 (1928). See also Willstaedt, SP 118,196.

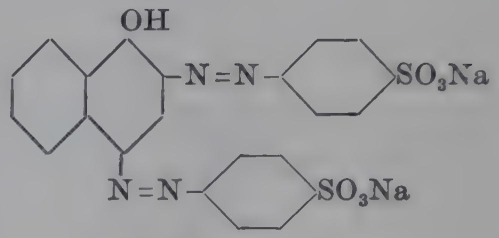
[4] See p. 480.

[6] See p. 480.

Black A (BASF; CI 241) is obtained from S-acid (sulfanilic acid $\xrightarrow{\text{acid}}$ S-acid $\xleftarrow{\text{alk.}}$ α-naphthylamine).

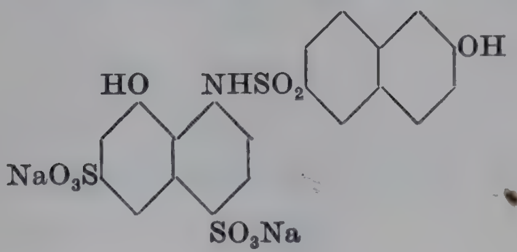


Acid Brown R

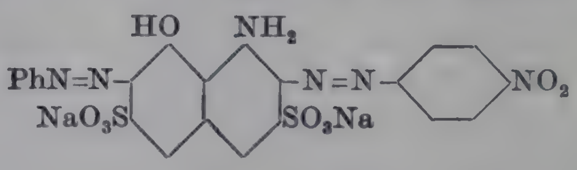


Fast Brown G

Acid Anthracene Red 3BL (IG), which is applicable to wool by the afterchrome or metachrome process, has only moderate fastness to light and washing. It is prepared by coupling two moles of a mixture of diazotized aniline (26%) and *o*-toluidine (74%) with (II), the condensation product of Schaeffer acid chloride and K-acid.[2] A very important second component for primary disazo dyes is H-acid. Naphthol Blue Black (C; CI 246) (*p*-nitroaniline $\xrightarrow{\text{acid}}$ H-acid $\xleftarrow{\text{alk.}}$ aniline) is a level dyeing, widely used acid dye. In admixture with yellow, orange and red acid dyes for shading purposes, it is the essential constituent of most of the black acid dyes on the market. Manufacturing details for Naphthol Blue Black (Amido Black 10B, IG) are as follows:[2] *p*-nitroaniline (260 kg.) in water (1200 l.) is mixed with sodium nitrite (132 kg.), and the suspension is run into a solution of sodium nitrite (1.2 kg.) and 19.5°Bé. hydrochloric acid (530 l.) in water (4000 l.) and ice (500 kg.), keeping the temperature at 10°. The diazonium solution is run through a Schibler filter into the coupling vat containing ice (1000 kg.). H-acid (485 kg.) dissolved in water (2600 l.) is run into the diazonium solution during 1–2 hours with stirring. Coupling is complete in 3 hours. Meanwhile, aniline (165 kg.) is diazotized in water (300 l.), ice (1500 kg.), and 19.5° Bé hydrochloric acid (440 l.) with sodium nitrite (124 kg.). The monoazo dye is dissolved by adding 40% (volume) caustic soda solution (360 l.), and cooled with ice (3000 kg.). Diazotized aniline is run in, followed immediately by 20% soda solution (1800 l.) added in 2–3 minutes. After 6 hours, the batch is salted to 9½% on the volume, stirred overnight and filtered (yield 1920 kg.). Neither the acid nor the



(II)



Naphthol Blue Black

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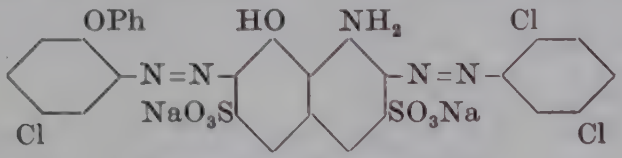
[2] See p. 480.

alkaline coupling apparently proceeds to completion under manufacturing conditions, and red monoazo dyes are present in the commercial product; the monoazo dyes modify the green-black shade of the pure disazo dye Estimation of the disazo dye by titanous chloride titration is complicated by the presence of the monoazo dyes, and it has been suggested[21] that a combination of spectrophotometric and titanous chloride titer methods is satisfactory for specifying a standard commercial type, since where the two methods agree the result is also in agreement with the usual dyeing test.

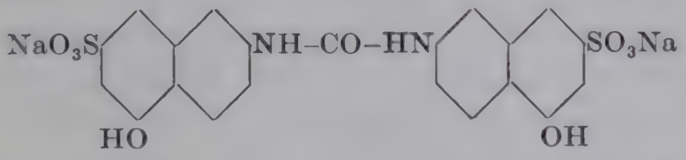
Replacing aniline by sulfanilic acid in the preparation of Naphthol Blue Black, the product is Blue Black NSF (IG);[2] and by *o*-aminodiphenyl ether, it is Naphthylamine Black 5GL (IG).[6] Cresol Black 6B (IG) is (*o*-chloroaniline $\xrightarrow{\text{1. acid}}$ H-acid $\xleftarrow{\text{2. alk.}}$ aniline).[6] Reduction of the nitro to the amino group in Naphthol Blue Black gives a dark green dye, Azo Dark Green A (Gy; CI 247) (Amido Dark Green B, IG),[2] useful for shading purposes.



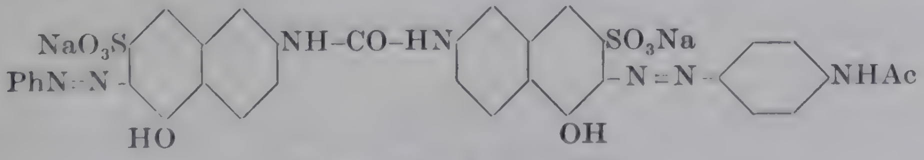
Sulphon Acid Green 2BL

Sulphon Acid Green 2BL (IG) and Diamond Green SS (2,5-dichloroaniline $\xrightarrow{\text{acid}}$ H-acid $\xleftarrow{\text{alk.}}$ α-naphthylamine) are other green wool dyes, using H-acid as dual coupling component.[2] CI 302 mentions Diamond Green SS as a mixture of Diamond Green B and Patent Blue.

The disazo dyes from carbonyl-J-acid (III), which are direct cotton dyes, may be regarded as primary disazo dyes in which the second component is a urea derivative, but they are sometimes classed separately (see Chapter XVI), since it is possible, and in fact more practicable in many cases, to prepare them by condensing phosgene with two moles of an aminoazo dye. The substantivity of these dyes for cellulose is due to their derivation from J-acid and to the amide group. Benzo Fast Scarlet 4BS



(III)



Benzo Fast Scarlet 4BS

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[21] Appel, Brode and Welch, *Ind. Eng. Chem.* **18**, 627 (1926); Brode, *ibid.* 708.

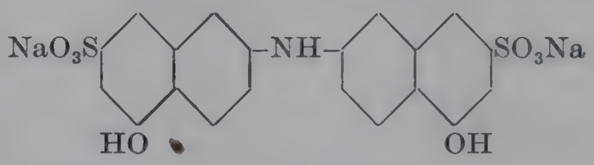
[2] See p. 480.

[6] See p. 480.

(By; CI 327) (aniline→III←*p*-aminoacetanilide) is similar in shade to Benzopurpurine 4B; and other largely used dyes with various commercial names (Benzo Fast Orange, Direct Fast Orange, etc.) (CI 326) are prepared by minor changes in the diazonium components (substituted anilines and naphthylamines). Examples[2, 6] are Benzo Fast Orange F3R (IG) (*o*-toluidine-5-sulfonic acid→III←*o*-toluidine); Benzo Fast Orange WS (IG) (aniline→III←*p*-aminobenzoic acid); Benzo Fast Scarlet 4BA (IG) (*o*-toluidine-5-sulfonic acid→III←*o*-anisidine); Benzo Fast Scarlet 8BS (IG) (naphthionic acid→III←*o*-anisidine+7.5% aniline); Benzo Fast Scarlet 8BA (Laurent acid ⇉ III); Diamine Fast Scarlet 7BH (Dahl acid→III←*o*-anisidine); and Benzo Fast Scarlet GS (aniline →III←Brönner acid). In comparison with the benzidine type of direct cotton dyes, derivatives of (III) have somewhat higher light fastness, but their main advantage is the complete absence of sensitivity to acids.

The use of thiocarbonyl-J-acid in place of J-acid has been the subject of patents; condensation products of J-acid with isophthalic and terephthalic acids have been mentioned.[5]

"Di-J-acid" (IV) was suggested (1899) as a component with two



(IV)

coupling positions for the preparation of disazo dyes, but commercial success was limited because of the inferior substantivity and fastness properties of the dyes compared to the carbonyl-J-acid dyes. An interesting difference between (IV) and (III) as intermediates for disazo dyes is the bathochromic character of the -NH- linking; the amide group insulates the two halves of the disazo dye. Thus Benzo Rhoduline Red B (IG) (aniline→IV←aniline) is bluish red in shade,[2] while the urea analog is orange. Benzo Rhoduline Red 3B (IG) is the analog made by using a mixture of 27% of *o*-anisidine and 73% of mixed xylidines.[2] Both the dyes have very poor light fastness (1). Diazo Bordeaux 7B has been stated to be (monoformyl-*m*-phenylenediamine ⇉ IV; hydrolyze the formyl groups).[6]

AMINOAZOBENZENE AND AMINOAZONAPHTHALENE DERIVATIVES

Sometimes classified as "unsymmetrical secondary disazo dyes," the distinctive feature of the dyes in this group is their preparation: (1) coupling a diazonium salt with a primary aromatic amine having a free *p*-position; and (2) diazotizing the resultant *p*-aminoazobenzene derivative and coupling

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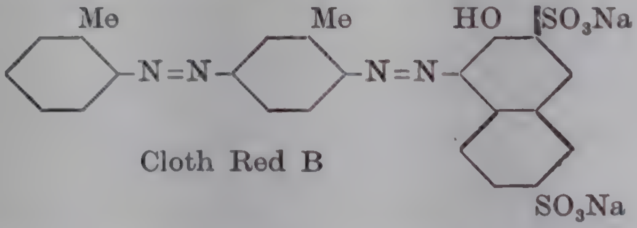
[2,6] See p. 480.

[5] See p. 480.

it with a suitable end component (A⟶M⟶E). Structurally most of these dyes are 1,4-disazo derivatives of benzene or naphthalene. In their dyeing properties they belong to the acid, acid mordant and direct cotton dyes, and in general they possess good fastness to light. The shades available in the series are red, through blue to black. The dark blues and blacks of the series, which have excellent fastness properties, need some care during dyeing to avoid unlevel results, since they are liable to undergo hydrolysis by the action of sulfuric acid.[22]

Cloth Red B (GrE; CI 262) (*o*-toluidine⟶*o*-toluidine⟶R-acid) and the aniline analog (Cloth Red 2R) (CI 253) are acid dyes. Cloth Red G (IG) is (4-aminoazobenzene⟶NW-acid+5% R-acid); New Red 5R (IG) is (4-aminoazobenzene-4′-sulfonic acid⟶mixture of Schaeffer and crocein acids). Brilliant Crocein M (By; CI 252) (aniline⟶aniline⟶G-acid) is level dyeing and has high fastness to light, but is not fast to severe washing. Brilliant Crocein 9B is (amido-G-acid⟶*o*-toluidine⟶G-acid). Cloth Scarlet G (Nietzki, 1878; CI 275) (sulfanilic acid⟶aniline⟶β-naphthol)



Cloth Red B

is a useful dye for wool and chrome-mordanted wool, and for jute, the shades possessing high fastness to washing. Crocein Scarlet 7B (4-amino-3,2′-dimethylazobenzene-4′-sulfonic acid⟶Schaeffer acid)[6] and Crocein Scarlet 10B (sulfanilic acid⟶*o*-anisidine⟶crocein acid)[6] have good light fastness. A few of these acid disazo dyes are useful for the preparation of lakes. Thus, Lithol Bordeaux R and B (IG) are made from the azo dyes obtained by coupling NW-acid with diazotized aminoazobenzene and *o*-aminoazotoluene respectively.[1]

Scarlet Red (Biebrich Scarlet Red) (*o*-aminoazotoluene⟶β-naphthol) and Scarlet Red Sulfonate (Ponceau 3RB; Biebrich Scarlet; CI 280) (4-aminoazobenzene-3,4′-disulfonic acid⟶β-naphthol) have therapeutic uses in burns and wounds, because of their property of stimulating the proliferation of epithelial cells.

Dyes derived from aminoazobenzenes as the diazonium components become applicable to cotton if γ-acid or J-acid or one of its *N*-acyl derivatives or *m*-phenylenediamine is the end component; the J-acid dyes are however much more substantive than the γ-acid and *m*-phenylenediamine derivatives. J-Acid is an azo dye intermediate of great importance by virtue of its distinctive property of imparting marked substantivity for cotton to the azo dyes of which it is a component. It is used in a few cases for the preparation of the benzidine type of disazo dyes, but since the benzidine dyes are substantive to cotton irrespective of the nature of the second components, the greater value of J-acid is as an end component in the preparation of disazo and trisazo dyes from aminoazobenzene and aminoazonaphthalene derivatives as diazonium components. Many commercially valuable dyes are therefore prepared by the schemes (A⟶M⟶J-acid); and (A⟶M^1⟶M^2⟶J-acid). In place of J-acid, an *N*-substituted J-acid (particularly the *N*-benzoyl and *N*-phenyl derivatives) may be employed. J-acid dyes are characterized by their brightness and level-dyeing power. The J-acid component itself has not been found to be a special contributing factor to fastness, and the fastness properties in the series are more dependent on the number of azo groups, the suitability for fastness-improving aftertreatments, and other factors. Several of the direct cotton dyes of the Sirius range (IG) which have very good fastness to light belong to this class.

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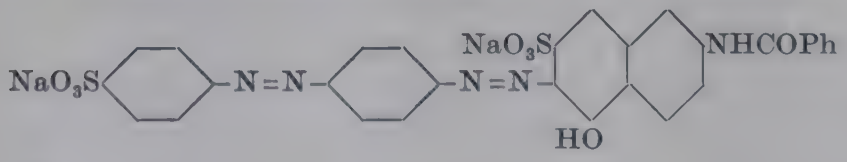
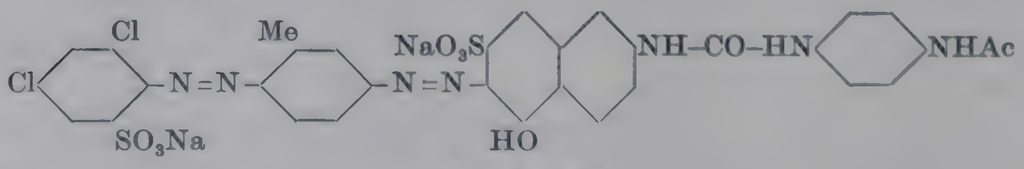
[22] Rowe and Dangerfield, *J. Soc. Dyers Colourists* **52**, 49 (1936).
[6] See p. 480.
[1] See p. 480.

Brown dyes for cotton are obtained by using *m*-phenylenediamine as the end component. Benzo Brown D3G extra (By; CI 273) (sulfanilic acid⟶aniline⟶*m*-phenylenediamine) however is also applicable to wool. Other examples are Cotton Brown A (IG) (naphthionic acid+Cleve-7-acid ⟶ α-naphthylamine ⟶ *m*-phenylenediamine) and Sirius Corinth B (aniline-2,5-disulfonic acid⟶Cleve-7-acid⟶4-nitro-*m*-phenylenediamine).[6]

Benzo Fast Red 8BL (By; CI 278) (Sirius Red 4B, IG)[2] (sulfanilic acid ⟶aniline⟶benzoyl-J-acid) is an important dye which is level dyeing and has good fastness to light (5); the fastness to washing is improved by dichromate-copper sulfate aftertreatment.[23] Cloth Scarlet G may be compared with Benzo Fast Red 8BL; the former is an acid color for wool



Benzo Fast Red 8BL



Sirius Red 5B

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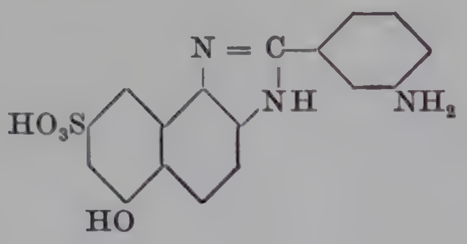
[6] See p. 480.

[2] See p. 480.

[23] See p. 494.

and the latter a substantive cotton color, but the structural difference is only in the end components, β-naphthol in one case and benzoyl-J-acid in the other. Other red dyes of this type are Sirius Red 5B, Sirius Ruby Red B and R (4-chloroaniline-2-sulfonic acid→*o*-toluidine→acetyl-J-acid) and Sirius Red 2B (3-chloro-*o*-toluidine-5-sulfonic acid→aniline →benzoyl-J-acid).[6]

For several of the direct cotton dyes of the Diamine range (IG), the imidazole (I) from J-acid is used as the middle component. Examples[6] are Diamine Fast Scarlet GFF (aniline→I→NW-acid); Diamine Fast Scarlet 2G (aniline→I→Schaeffer acid); and Diamine Brilliant Ruby Red S (*o*-anisidine→I→Chicago acid). Benzoform Scarlet B, suitable for formaldehyde aftertreatment,[23] is also of this type (*p*-xylidine→I→ resorcinol).



(I)

The bathochromic effect of *C*-alkyl groups and of *N*-phenylation is seen in Brilliant Benzo Fast Violet 2RL (IG) (*m*-4-xylidine-5-sulfonic acid→ *p*-xylidine→phenyl-J-acid);[2,5] a bluer shade of violet results in Sirius Violet BB (IG), prepared by a similar scheme in which *p*-xylidine is replaced by cresidine.[2] Diamine Fast Violet RBN (IG) is (1-naphthylamine-2-sulfonic acid→cresidine→phenyl-J-acid).[6] Other violets of this type are Benzo Violet BL extra (IG) (*o*-toluidine→Cleve-6-acid→J-Acid + 5% phenyl-J-acid); Brilliant Congo Violet R (IG) (2-naphthylamine-4,8-disulfonic acid→*p*-xylidine→phenyl-J-acid) and Brilliant Benzo Violet B (sulfanilic acid→cresidine→phenyl-J-acid). Sirius Bordeaux 5B (IG) (4-chloroaniline-2-sulfonic acid→*p*-xylidine→acetyl-J-acid)[2] is a direct cotton dye with good light fastness (5), but poor fastness (1) to water and washing. In Benzo Bordeaux 6B (IG) (aniline$\xrightarrow{\text{alk.}}$J-acid$\xrightarrow{\text{alk.}}$J-acid), J-acid is employed as both the middle and end components.[2] H-acid may be used as the first component in preparing useful members of this series. Brilliant Benzo Violet 2RL (By) (H-acid→*m*-toluidine→ phenyl-J-acid),[14] and Benzo Fast Heliotrope BL (By; CI 319) (H-acid →α-naphthylamine→phenyl-J-acid) are bright direct dyes for cotton with high fastness to light; using cresidine as the middle component in this scheme, a blue direct cotton dye, Sirius Supra Blue F3R (IG), with very good light fastness (5–6) is obtained.[2] Brilliant Congo Blue 5R and BFL (IG) are (2-naphthylamine-4,8-disulfonic acid⟶cresidine⟶phenyl-J-acid) and (1-naphthylamine-4,7-disulfonic acid⟶α-naphthylamine⟶phenyl-J-acid). A dye in which J-acid is the first component, and M is a benzene derivative, is Diamine Fast Violet BBN (C; CI 325) (J-acid⟶cresidine⟶phenyl-J-acid). The shade on cotton has moderate fastness to light and poor fastness to washing, the latter being improved by coupling on the fiber with diazotized *p*-nitroaniline. Aftertreatment with copper sulfate has also been recommended.[23]

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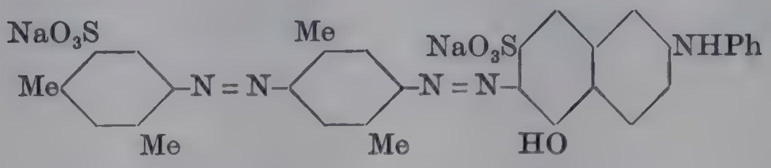
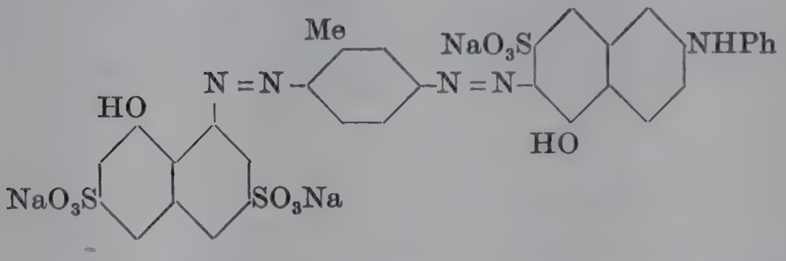
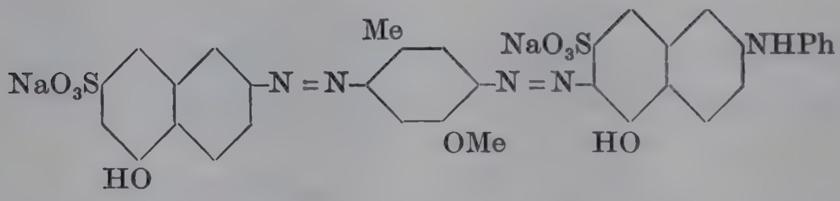
[6] See p. 480. [23] See p. 494. [2,5] See p. 480. [14] See p. 490.



Brilliant Benzo Fast Violet 2RL

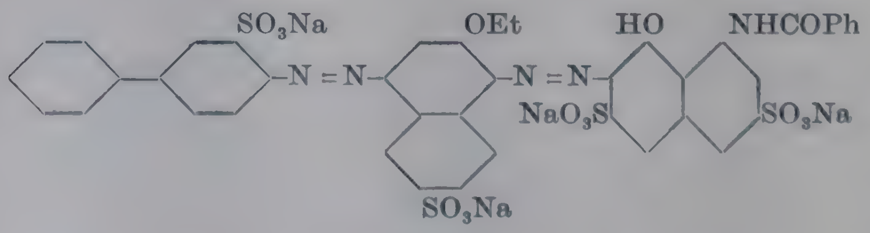


Brilliant Benzo Violet 2RL



Diamine Fast Violet BBN (C)

Green dyes in the series are Brilliant Benzo Fast Green GL (IG) (4-aminodiphenyl-3-sulfonic acid⟶1-amino-2-ethoxynaphthalene-6-sulfonic acid⟶benzoyl-H-acid), and Brilliant Benzo Green B (IG) (2-naphthylamine-8-sulfonic acid ⟶ 1-amino-2-ethoxynaphthalene⟶1,8-dihydroxy naphthalene-4-sulfonic acid).[2] The second coupling in both the cases is sluggish and is carried out in aqueous pyridine. These are bright, level-dyeing dyes, but the shades have low fastness (washing 1–2; light 3–4).



Brilliant Benzo Fast Green GL

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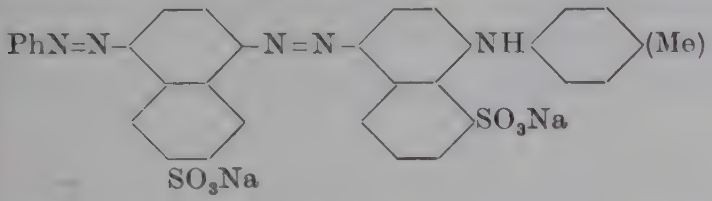
[2] See p. 480.

[23] See p. 494.

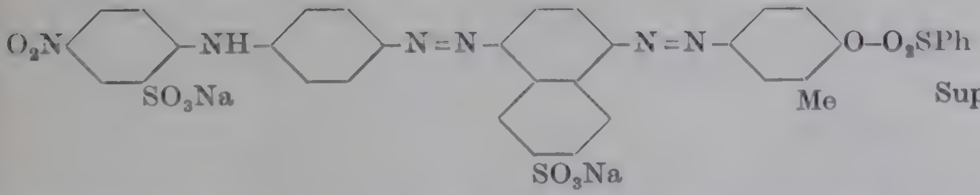
γ-Acid as the end component is useful for gray and black direct cotton dyes with good light fastness. Neutral Gray G (AGFA; ST 551) (aniline → α-naphthylamine $\xrightarrow{\text{alk.}}$ γ-acid) dyes cotton a pure gray. Two other examples are Benzo Fast Black (By) (5-aminosalicylic acid → α-naphthylamine $\xrightarrow{\text{alk.}}$ γ-acid) and Zambesi Black D (AGFA) (*p*-phenylenediamine → cresidine $\xrightarrow{\text{alk.}}$ γ-acid).[14]

Valuable blue dyes for wool are obtained by using a benzene derivative as A in the scheme (A → M → E), while M and E are naphthalene derivatives, M being α-naphthylamine or the Cleve acids, and E being *N*-phenyl or *N*-*p*-tolyl-peri acid. Sulphon Cyanine G and 3R (IG) (aniline → Cleve acids → *p*-tolyl-peri acid or phenyl-peri acid), GR extra (CI 288–9) and 5R (metanilic acid → α-naphthylamine → *p*-tolyl-peri acid or phenyl-peri acid), are important dyes of this type,[2, 6] which have high fastness to light (5–6) and milling (3–4). Outstanding fastness to light and sea-water is claimed for the blue disazo dye (2-methyl-5-aminophenyl 3-sulfophenyl sulfone → α-naphthylamine → *p*-tolyl-peri acid).[24]



Sulphon Cyanine 3R and G

Supranol Brown 5R (IG) (4-nitro-4′-aminodiphenylamine-2-sulfonic acid $\xrightarrow{\text{acetic acid soln.}}$ Cleve acids $\xrightarrow{\text{alk.}}$ *o*-cresol; then esterify the hydroxyl group with benzenesulfonyl chloride), like the Polar colors containing arylsulfonyl ester groups, has good fastness properties.[1] New dyes of the Polar type mentioned in patents are represented by the schemes (2-amino-4-sulfo-2′-methyldiphenyl ether → 2R-acid → phenol) and (*p*-phenylenediamine-*o*-sulfonic acid $\xrightarrow{\text{acid}}$ γ-acid → phenol), the final stage in both cases being, as usual, esterification of the hydroxyl group by means of *p*-toluenesulfonyl chloride; the first is a red dye and the second violet. Disazo dyes of the type (sulfo-*o*-tolyl 1-amino-2-benzenesulfonate → 1-naphthylamine → phenyl-peri acid) are fast blue dyes for wool.[25]



Supranol Brown 5R

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[14] See p. 490.

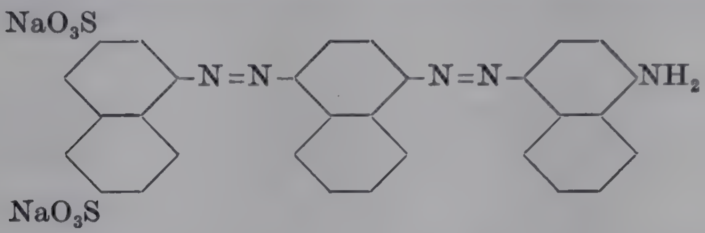
[2,6] See p. 480.

[24] Geigy, SP 217,950; see also SP 217,951–7.

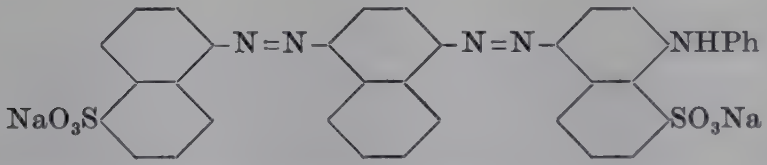
[1] See p. 480.

[25] Geigy, BP 502,309; 507,967; 585,997.

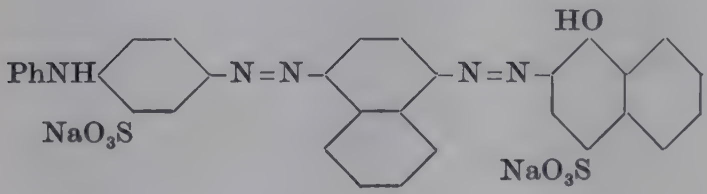
If in disazo dyes of this type suitable naphthalene intermediates are used, black dyes are obtained. An example is Naphthylamine Black D (Weinberg, 1888; CI 308) (Freund acid⟶α-naphthylamine⟶α-naphthylamine) which is an acid color. A black in which the end component is a naphtholsulfonic acid is Naphthol Black B (AAP, C; CI 315) (β-naphthylamine-6,8-disulfonic acid ⟶ α-naphthylamine ⟶ R-acid). Another important black dye for wool is Sulphon Cyanine Black B (By; CI 307) (Laurent acid⟶α-naphthylamine⟶phenyl-peri acid); the 3B (or 8B) brand is prepared by using *p*-tolyl-peri acid as the end component.[6] The production of a black is also possible by replacing the naphthylamine derivative used as first component by a diphenylamine derivative, Nerol B and 2B (AGFA; CI 305 and 304) (4-aminodiphenylamine-2-sulfonic acid⟶α-naphthylamine⟶R-acid or NW-acid) being important examples. Improved level-dyeing properties are obtained if β-naphthol-4-sulfonic acid is used as end component.[26] Two naphthalene residues are adequate for producing a black, if the dye has structural features such as a 1,8-dihydroxynaphthalene end component. Examples are Sulphon Black R (By; CI 271 (aniline⟶Cleve acids⟶dioxy-S-acid) and Victoria Black B (IG) (sulfanilic acid⟶α-naphthylamine⟶dioxy-S-acid).



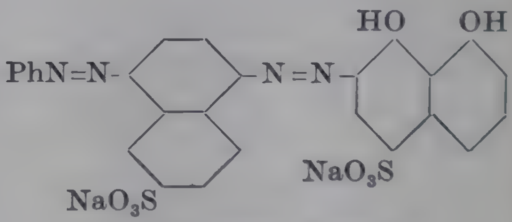
Naphthylamine Black D



Sulphon Cyanine Black B



Nerol 2B



Sulphon Black R

Nitrazol Black M (IG, 1941) yields fast shades on mixed materials (e.g., hosiery and knitting yarns of staple fiber and wool) by development on the fiber with diazotized *p*-nitroaniline.[3] In the scheme (A⟶M⟶E) by which it is prepared, A is the infrequently employed M-acid, and E is a mixture of half a mole each of S-acid and its *N*-benzoyl derivative.

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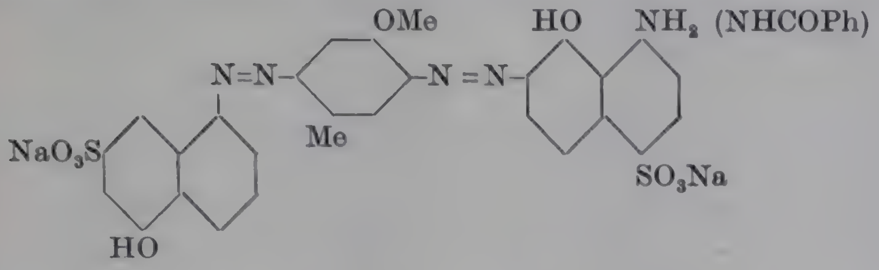
[6] See p. 480.

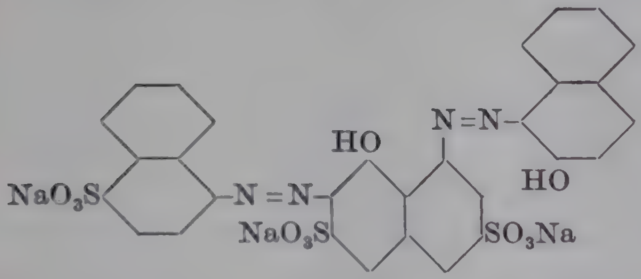
[26] Geigy, BP 473,525.

[3] See p. 480.



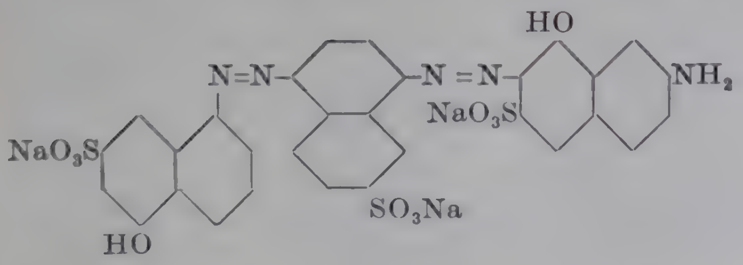
Nitrazol Black M

The use of H-acid as M in the scheme (A⟶M⟶E) is exemplified by the deep black wool color, Fast Sulphon Black F (S; CI 306) (naphthionic acid$\xrightarrow{\text{alk.}}$H-acid⟶β-naphthol). A deep green dye for leather is obtained by using resorcinol as the end component.[27]



Fast Sulphon Black F

Autazol Chrome Black BA (IG) (M-acid⟶Cleve-7-acid$\xrightarrow{\text{alk.}}$γ-acid) is useful for the production of fast black shades on mixed yarns of spun rayon and wool.[3] Further examples of Autazol dyes are quoted elsewhere, and



Autazol Chrome Black BA

their characteristic property is their simultaneous affinity for both spun viscose and wool, while cellulose acetate remains undyed. The affinity for cellulose rayon is due to the derivation of the dyes from γ-acid or J-acid. After dyeing from an ammonium sulfate-sodium sulfate bath, Autazol Chrome Black BA is developed by an interesting method. The amino group in the γ-acid residue is diazotized, but the diazonium salt is not coupled in the usual manner with a new end component; the diazotized dye on the fiber is treated with ammonia, when coupling apparently takes place in the available position of the M-acid residue. A greenish blue-black shade with excellent fastness (light 6–7, milling 4–5) is produced;

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[27] Atkinson, Mendoza and ICI, BP 557,373.

[3] See p. 480.

afterchroming leads to a fuller, deeper and somewhat faster black. Autazol Chrome Navy Blue BRA, which gives bright navy blue shades on union fabrics of spun rayon and wool, is the analog of Autazol Chrome Black BA, in which the end component is J-acid.

DERIVATIVES OF TETRAZOTIZED DIAMINES

The general scheme of preparation ($E^1 \leftarrow D \rightarrow E^2$) of this large and important group of azo dyes is to tetrazotize benzidine or one of its derivatives, or other *p*-diamines of a definite type, or certain *m*-diamines, and couple the bisdiazonium salt with two moles of the same or one mole each of two different second components. The dyeing property which distinguishes this class of disazo dyes, of which the first example was Congo Red (Böttiger, 1884), is their substantivity for cellulose fibers. The nature of the dyeing process for direct cotton dyes indicates that fastness to vigorous washing is not to be expected; the benzidine type disazo dyes have in addition poor light fastness. Nevertheless, in view of the relatively low cost of the dyes and their adequacy for some purposes, direct cotton dyes of the benzidine class have been extensively investigated and continue to be manufactured. All the disazo direct cotton dyes are not derived from the benzidines or analogous diamines, but the great majority of the cheap, general utility dyes are, and the main exceptions in this class of product are the dyes derived from J-acid and γ-acid. Except for a few copper complexes of dyes derived from dianisidine which have good fastness to light, the fast-to-light direct cotton colors are not of the benzidine type.

Among the various types of diamines, which are suitable for the preparation of direct cotton colors, benzidine and its derivatives (notably *o*-tolidine and dianisidine) are by far the most important technically; the disazo dyes from diaminodiphenylurea, diaminostilbene, etc., are limited in number and their special function is to fill the gaps in the shades obtainable from the benzidine dyes. A wide range of shades is available in the benzidine series of disazo dyes, but there is an absence of greens and deep blacks, for which the introduction of a third azo group by synthesis in substance or by an aftertreatment process becomes necessary. The technically important yellow dyes are not made from benzidine or the substituted benzidines, but from diaminodiphenylurea and diaminostilbene derivatives. Table II illustrates the shades on cotton produced by the disazo dyes obtained by coupling tetrazotized benzidine with various end components; and Table III illustrates the comparatively minor variations in shade which are obtained when benzidine and other *p*-diamines are tetrazotized and coupled with two moles of the same end component (naphthionic acid).

TABLE II

SHADES (ON COTTON) OF DISAZO DYES FROM BENZIDINE

*E*¹	*E*²	*Dye*	*Shade*	*CI No.*
Salicylic acid	Salicylic acid	Chrysamine G	Yellow	410
Salicylic acid	γ-Acid*	Diamine Fast Red F	Yellowish red	419
Salicylic acid	Resorcinol	Cloth Orange	Orange	412
Salicylic acid	Naphthionic acid	Benzo Orange R	Orange	415
Salicylic acid	γ-Acid†	Diamine Brown M	Deep brown	420
Salicylic acid	J-acid	Direct Red J (Oxamine Red X)	Dark red	425
Naphthionic acid	Naphthionic acid	Congo Red	Red	370
m-Phenylenediamine	γ-Acid†	Diamine Brown V	Violet-brown	396
Naphthionic acid	NW-acid	Congo Corinth G	Brown-violet	375
Acid GR	NW-acid	Chlorazol Violet R	Violet	388
Crocein acid	Crocein acid	Bordeaux COV	Violet	385
γ-Acid*	γ-Acid*	Diamine Violet N	Violet	394
γ-Acid†	γ-Acid†	Diamine Black RO	Gray-violet	395
Chromotropic acid	Chromotropic acid	Dianil Blue R	Reddish blue	390
H-acid†	H-acid†	Benzo Blue BB	Blue	406
H-acid†	N-Ethyl-γ-acid†	Diphenyl Blue Black	Deep blackish blue	402
N-Ethyl-γ-acid†	N-Ethyl-γ-acid†	Diphenyl Fast Gray B	Bluish gray to black	403

*Acid-coupled. †Alkali-coupled.

TABLE III

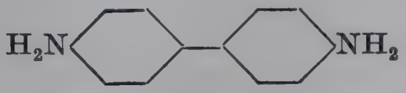
SHADES (ON COTTON) OF DYES FROM BENZIDINE AND OTHER DIAMINES USING 2 MOLES OF NAPHTHIONIC ACID AS THE END COMPONENTS

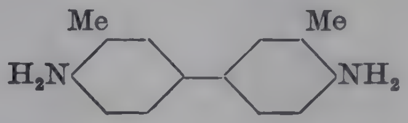
Diamine	*Dye*	*Shade*	*CI No.*
Benzidine	Congo Red	Red	370
o-Tolidine	Benzopurpurine 4B	Scarlet	448
Dianisidine	Benzopurpurine 10B	Carmine red	495
o-Dichlorobenzidine	Dianol Red 2B (Benzo Red 10B)	Bluish red	434
4,4′-Diaminodiphenylurea	Salm Red	Flesh color to brownish orange	347
4,4′-Diaminodiphenylthiourea	Salmon Red	Orange red	351
1,5-Diaminonaphthalene	Naphthylene Red	Red	526

Structural features of diamines as first components for direct cotton dyes. These diamines belong to five main types. In contrasting them with the closely related diamines which are stated as not leading to substantive dyes, it is to be noted that complete absence of dyeing power is not necessarily intended. There is no sharp line of demarcation between substantive and unsubstantive dyes, and the basis for the distinction is the possession of adequate substantivity for practical dyeing purposes. The terms " substantivity " and " substantive dyes " in this section refer only to cotton and other cellulose fibers.

(*a*) Benzidine (I) and its *o*-disubstituted derivatives,[28] particularly *o*-tolidine (II), dianisidine (III) and *o*-dichlorobenzidine (IV). These yield substantive dyes regardless of the nature of the second components.

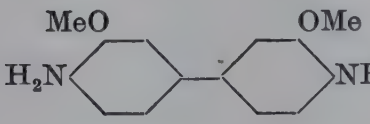
(I)

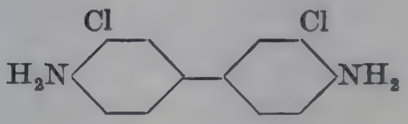




(II)

(III)



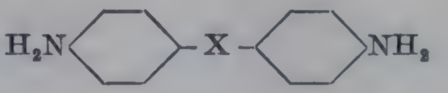


(IV)

The corresponding *m*-substituted compounds do not yield substantive dyes.

(*b*) 1,4- and 1,5-Diaminonaphthalene. In contrast to the diamines mentioned in (*a*), (*c*) and (*d*), 1,4-naphthylenediamine yields substantive dyes only if at least one of the second components is J-acid, γ-acid or *m*-phenylenediamine; but the 1,5-isomer is more favorable to substantivity and yields a substantive dye with two moles of naphthionic acid.

(*c*) 4,4′-Diamines of the type (V), in which X is NH, CH=CH, NH–CO–NH, NH–CS–NH or N=N; i.e., the *p*-diamines of diphenylamine, stilbene, diphenylurea, diphenylthiourea and azobenzene. Diamines of the type (V) in which X is $O–(CH_2)_{1-6}–CO–NH–(CH_2)_{2-10}–NH–CO–(CH_2)_{1-6}–O$ or $CO–NH–(CH_2)_{2-18}–NH–CO$ have been stated to yield substantive dyes.[29] A diamine in which the bridge is the *m*-phenylene radical is bis-*p*-aminobenzoyl-*m*-phenylenediamine; tetrazotized and coupled with 1-(*m*-aminophenyl)-3-methyl-5-pyrazolone, the dyes may be further tetrazotized and developed on the fiber, giving fast yellow shades.[30]



(V)

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[28] In benzidine derivatives, *o* and *m* are with reference to the amino groups; but numbers start from the diphenyl linkage; thus *o*-tolidine-6,6′-disulfonic acid is 4,4′-diamino-*m*-ditolyl-6,6′-disulfonic acid.

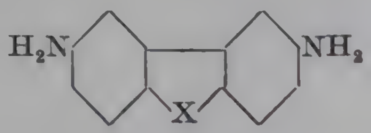
[29] du Pont, USP 2,161,628; 2,286,391–2; 2,164,785–6.

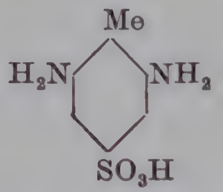
[30] Rossander and du Pont, USP 2,148,134–5.

The 4,4′-diamines of diphenylmethane, dibenzyl and diphenyl sulfide (V; X = CH_2; CH_2–CH_2; S), do not lead to substantive dyes; but some disazo dyes of this type are useful as acid colors for wool. The preparation of substantive dyes from iodinated diaminodiphenylmethane has been claimed;[31] coupled with Chicago acid and other naphthol or aminonaphthol sulfonic acids, dyes of the Chicago Blue type have been prepared.

(*d*) 3,6-Diamino derivatives of carbazole, diphenyleneoxide, fluorene and diphenylene sulfone (VI; X = NH, O, CH_2 or SO_2), and of similar tricyclic compounds. These may be regarded as *m*-disubstituted benzidine derivatives, in which the two *m*-substituents have been cyclized; the substantivity of the dyes derived from these diamines and the diamines listed in (*a*) and (*c*) has been associated with their coplanarity, while the analogous diamines which yield unsubstantive dyes are nonplanar.[32]

(VI)

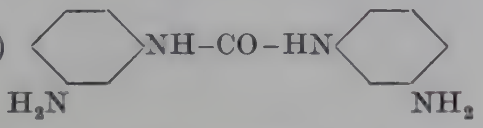


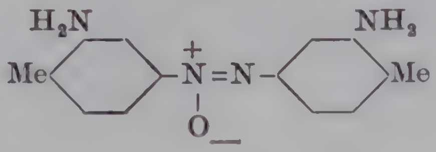


(VII)

(*e*) 2,6-Diaminotoluene-4-sulfonic acid (VII) is an interesting example of a *m*-diamine, which gives substantive dyes. There are also a few diamines which lead to substantive dyes, but in which the amino groups are *meta* to the points of linkage of the two benzene rings with the bridging group. Examples are 3,3′-diaminodiphenylurea (VIII) and diaminoazoxytoluene (IX).

(VIII)

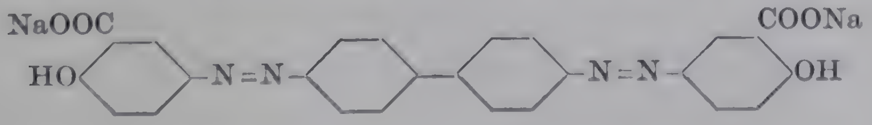




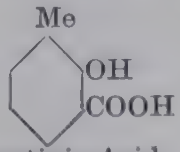
(IX)

DIRECT COTTON DYES FROM BENZIDINE AND ITS DERIVATIVES

Chrysamine G (Frank, 1884; CI 410) (benzidine $\rightrightarrows$ salicylic acid, 2 moles) was the first yellow direct cotton dye, and is still employed for the same purpose, although by virtue of its being an azosalicylic acid it has mordant dyeing properties. For this reason, however, the dye is sensitive to iron and other metals, which dull the shades. Chrysamine R (By;



Chrysamine G



Cresotinic Acid

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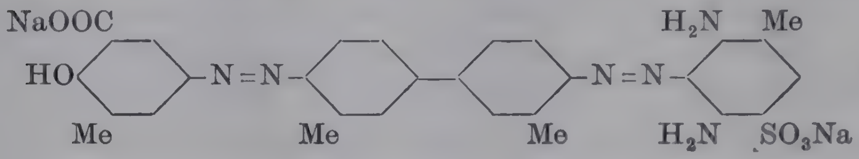
[31] Ward, Blenkinsop and Co., BP 540,455.

[32] For a full discussion see Chapter XLI in Vol. II.

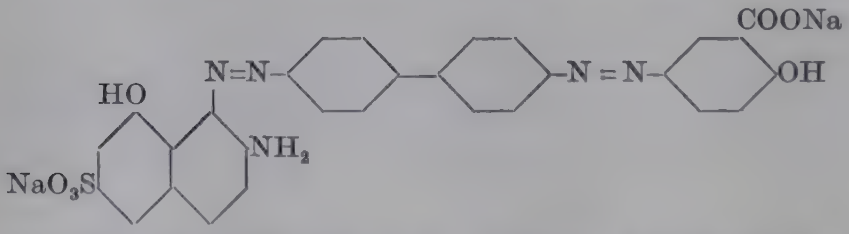
CI 480), the analog from *o*-tolidine, is redder in shade. Both the Chrysamines have better light fastness than is usual among the benzidine dyes, and are useful in calico printing. Replacing one mole of salicylic acid by *m*-aminophenol-*p*-sulfonic acid, a useful orange dye, Diamine Orange B (By; CI 409) (Brilliant Direct Orange G, IG) is obtained; aftertreatment with copper sulfate changes the shade to brown.[33]

Pyramine Orange R (BASF; CI 440) is (benzidine-*o*-disulfonic acid ⇉ 4-Nitro-*m*-phenylenediamine, 2 moles). Toluylene Orange G (By; CI 478) (Pluto Orange G) dyes cotton an orange yellow, converted into a red-brown by developing on the fiber with diazotized *p*-nitroaniline; since there is no available position for coupling, the replacement of a carboxyl or sulfonic group must be assumed.



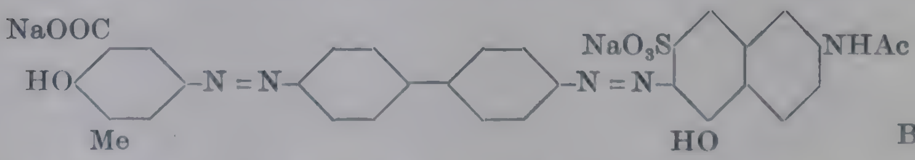
Toluylene Orange G

By employing a benzene and a naphthalene derivative as the two second components, several useful dyes are obtained. Benzo Orange R (By) (salicylic acid + 10% cresotinic acid ← benzidine → naphthionic acid + 10% Brönner acid) is a useful direct cotton dye, as well as a chrome-mordant dye for wool.[6] Congo Orange G (CI 377) is (amido-R-acid ← benzidine → phenol; ethylate); Diamine Orange F (IG)[1] is constituted similarly, but a mixture of amido-R-acid (90%) and Brönner acid (10%) is used.[2]



Diamine Fast Red F

Oxamine Brilliant Red B is (Phenol-3-sulfonic acid ← benzidine → J-acid).[6] Benzo Fast Red GL (By) (salicylic acid ← benzidine → 2,5-dihydroxynaphthalene-7-sulfonic acid)[6] has light fastness 3–4. Diamine Fast Red F (C; CI 419) is a direct cotton dye, as well as a widely used acid dye for wool on which it yields a fast red by afterchroming. Using



Benzo Fast Red 2B

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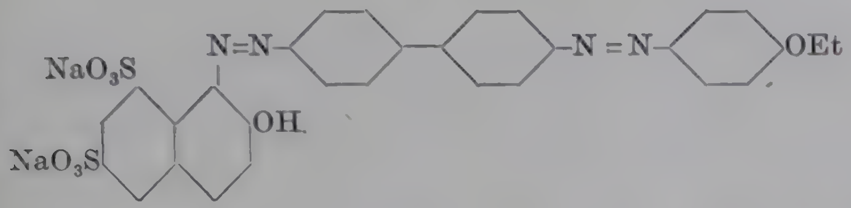
[33] According to Ref. 2, Diamine Orange B is a mixture of Primuline and dehydrothiotoluidinesulfonic acid → resorcinol ← aniline.

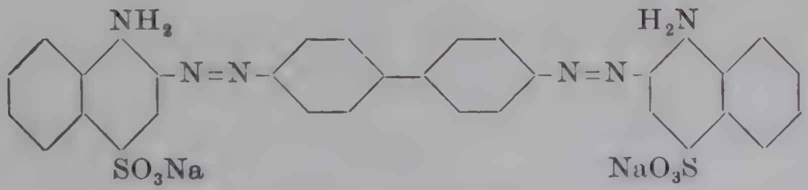
[6] See p. 480. [1] See p. 480. [2] See p. 480.

the same components, but carrying out the γ-acid coupling under alkaline conditions, the product is Diamine Brown M (C; CI 420), which is applicable to cotton, wool and silk, the fastness being improved by aftertreatment with dichromate or copper sulfate. Benzo Fast Red 2B (IG) dyes a bordeaux-red of good dischargeability.[34] A dye which is more useful as a wool color is Diamine Scarlet B (C; CI 382) (G-acid←—benzidine—→phenol, and then ethylate); replacing the etherification stage by esterification with *p*-toluenesulfonyl chloride gives Polar Red G (Gy; CI 430), a typical wool color inapplicable to cotton. Diamine Bordeaux S (IG) is (acid GR←—*o*-tolidine—→phenol; ethylate). Diamine Brown S (C) is (2R-acid←—benzidine—→*m*-phenylenediamine).



Diamine Scarlet B

Congo Red (benzidine ⇉ naphthionic acid, 2 moles), in spite of its low fastness, continues to be one of the bulk products of the dyestuff industry; in India it is used in larger quantities than any other dye with the exception of Sulfur Black. The dye is sensitive to acids, turning blue-violet with acetic acid and blue with mineral acids; Congo paper is used for testing for acidity. The fastness to washing and to acids may be improved by aftertreatments.[23] Chloramine Red 8BS (IG) (*o*-dichlorobenzidine ⇉ 2 moles amido-R-acid + 6% Brönner acid) has poor fastness to light (2), but good fastness to acid and alkali (3–4).[2] Oxamine Red 3B (IG) is (amido-R-acid←—benzidine—→J-acid). Congo Corinth G (AGFA) (naphthionic acid←—benzidine—→NW-acid) was the first mixed disazo dye to be marketed, and is still largely used, although it is even lower in fastness than Congo Red. The replacement of an amino group in Congo Red by a hydroxyl has a marked bathochromic effect, and Congo Corinth dyes cotton a brown-violet. Congo Rubine (AGFA; CI 376) (croccin acid←—benzidine—→naphthionic acid) is another cheap and useful dye, applicable to cotton, wool and silk. An interesting property of Congo



Congo Red

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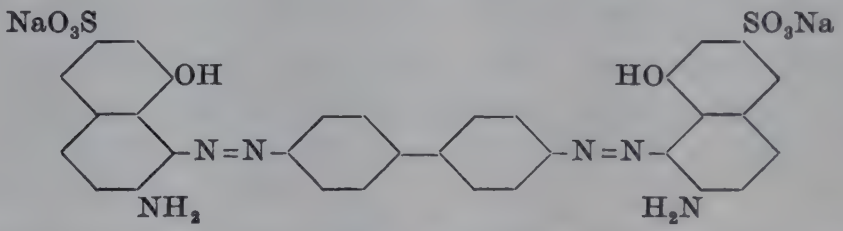
[34] *BIOS* **1088.**

[23] See p. 484.

[2] See p. 480.

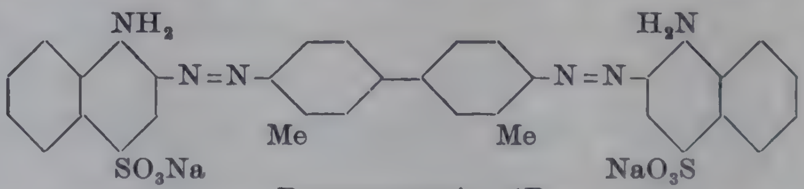
Rubine is the characteristic color change of the red colloidal solution to lilac on coagulation by the addition of sodium chloride; this salt sensitivity has been utilized for determining the protective colloidal action of surface-active compounds and other textile auxiliary agents in terms of a "Congo Rubine Number," the weight of sodium chloride required to change the color of a solution of Congo Rubine from red to lilac under standard conditions in presence of the substance under test.[35] Benzo Rubine HW (IG) (2-naphthylamine-5,7-disulfonic acid←—benzidine—→J-acid) is faster to light and acid than Congo Rubine.[2]

Bordeaux COV (AGFA; CI 385) (benzidine$\rightrightarrows$crocein acid, 2 moles) dyes violet on cotton and bordeaux-red on wool. Oxamine Bordeaux B (B) is (2-naphthylamine-6 or 7-sulfonic acid←—benzidine—→J-acid).[6] A violet (Trisulphon Violet B) (S; CI 387) with comparatively good fastness to washing is obtained by using one mole of β-naphthol and one of oxy-Koch acid as the second components. The largely used dye, Diamine Violet N (Gans, 1889; CI 394) is applicable to cotton, wool and silk, the fastness to light and other agencies being very good on the animal fibers. The replacement of one mole of γ-acid in Diamine Violet N by J-acid (alkali-coupled) gives Benzo Fast Violet R (IG).[2]



Diamine Violet N

Replacing benzidine by *o*-tolidine in the preparation of Congo Red, a bluer shade is obtained in Benzopurpurine 4B (By; CI 448), a largely used dye for pink on cotton and scarlet on wool. By using dianisidine in place of *o*-tolidine, the shade is still bluer in Benzopurpurine 10B, another important dye. Depending apparently on the purity of the intermediates, certain brands of the dye (e.g., Diamine Red 10B) (C; CI 495) have increased fastness to acids. Azo Blue (AGFA; CI 463) (*o*-tolidine$\rightrightarrows$NW-acid, 2 moles) dyes a red-violet rendered greener and faster to light by copper sulfate treatment.



Benzopurpurine 4B

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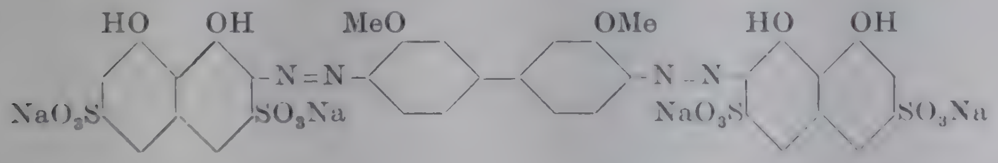
[35] Baudouin, *Melliand Textilber.* **17**, 654, 932 (1936); Ramachandran, Uppal and Venkataraman, *J. Soc. Dyers Colourists* **54**, 520 (1938).

[2] See p. 480.

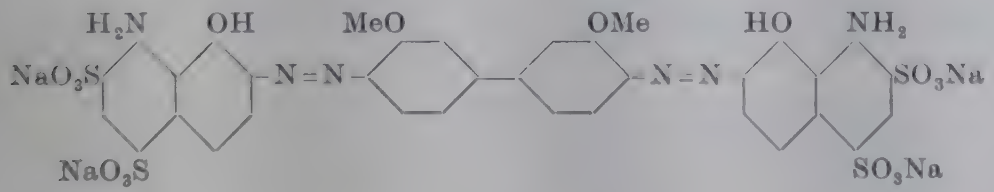
[6] See p. 480.

H-Acid, chromotropic acid and Chicago acid as second components lead to a series of blues. Benzo Blue BB (By) (Direct Blue 2B) (benzidine $\overset{\text{alk.}}{\rightrightarrows}$ H-acid, 2 moles) is used in spite of its poor fastness to light. Benzo Sky Blue (By; CI 520), the analogous dye from dianisidine, and Benzo Blue 3B (By; CI 477) from *o*-tolidine have also low fastness to light, but they are useful for some classes of cotton dyeing and printing. Several unsymmetrical disazo dyes from benzidine and *o*-tolidine, in which oxy-Koch acid or H-acid or chromotropic acid or S-acid is one component, and the other is β-naphthol, NW-acid, etc., are useful blues with varying tones of red. Examples are Trisulphon Blue R (S; CI 464) (oxy-Koch acid←—*o*-tolidine—→β-naphthol), a reddish blue with moderate fastness to washing after a dichromate treatment; Benzo Blue BX (By; CI 472) (H-acid←—*o*-tolidine—→NW-acid); and Benzo Blue 4R (IG; CI 391) (crocein acid←—benzidine—→S-acid). The dyes obtained from J-acid and H-acid by alkaline coupling can be altered in shade and rendered faster by diazotization of the primary amino groups and development with suitable components.[23]

Dianil Blue R (MLB; CI 390) (benzidine $\rightrightarrows$ chromotropic acid, 2 moles) has low fastness to washing and to light, somewhat improved by dichromate-copper sulfate treatment.[23] By coupling tetrazotized dianisidine with chromotropic acid and with Chicago acid (2S-acid), two important direct cotton dyes, Dianil Blue G (MLB; CI 508) and Diamine Sky Blue FF (C; CI 518) are obtained. Benzo Blue RW (By; CI 512) (Chicago acid ←—dianisidine—→β-naphthol) is applicable to cotton and wool; although like the other blues in the series the light fastness is poor, it is improved by copper sulfate treatment. Other examples of blues from dianisidine are: Oxamine Blue B (B; CI 515) (M-acid and NW-acid); Naphthamine Blue PBF (IG) (H-acid and phenyl-J-acid); Benzo Viscose Blue BB (IG) (crocein acid and S-acid); Brilliant Azurine B (IG) (acid GR and NW-acid); Triazol Pure Blue R (IG) (acid GR and phenyl-J-acid + J-acid).[6]



Dianil Blue G



Diamine Sky Blue FF

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[23] See p. 494.

[6] See p. 480.

Trypan Blue (MLB; CI 477) (*o*-tolidine $\underset{\longrightarrow}{\xrightarrow{\text{alk.}}}$ H-acid, 2 moles) and Trypan Red (MLB; CI 438) (benzidine-*o*-monosulfonic acid $\underset{\longrightarrow}{\longrightarrow}$ amido-R-acid, 2 moles) have been used in the chemotherapy of protozoal diseases.

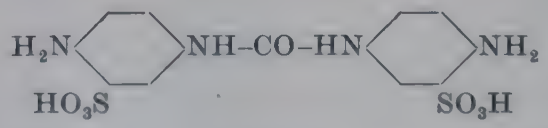
DYES FROM DIAMINES OTHER THAN BENZIDINE DERIVATIVES

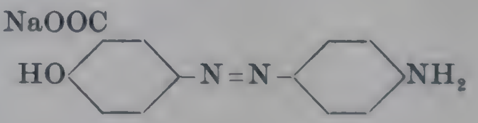
p-Phenylenediamine has to be tetrazotized under special conditions, and disazo dyes derived from it are therefore otherwise prepared. *p*-Aminoacetanilide is diazotized and coupled with an end component, the acetyl group is hydrolyzed, and the aminoazo compound again diazotized and coupled with a second mole of an end component. The aminoazo compound can also be prepared by sodium sulfide reduction of the dye (*p*-nitroaniline⟶E^1), but the aminoacetanilide route is preferred. In Para Black R (By; CI 339), E^1 is *m*-phenylenediamine, and E^2 is K-acid; it dyes cotton dark blue from an alkaline bath, which develops to a deep black, fast to washing, by coupling on the fiber with diazotized *p*-nitroaniline.[23]

Benzene-1,4-disazo dyes prepared by the scheme (A⟶M⟶E), in which M is aniline or an aniline derivative with a free *p*-position, are also *p*-phenylenediamine derivatives, but they have been treated earlier.

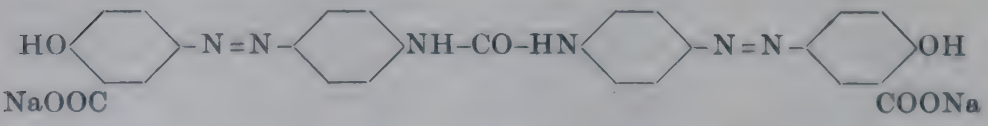
Dyes derived from diaminodiphenylurea are important direct cotton dyes, prepared by coupling tetrazotized 4,4′-diaminodiphenylurea (I) or its 3,3′-disulfonic acid (II) with suitable second components; or by phosgenating the appropriate aminoazo compound. They have good fastness to washing and a considerably higher grade of light fastness than the benzidine dyes. Coupling (I) with 2 moles of salicylic acid, the bright lemon-yellow cotton color, Benzo Fast Yellow 5GL (BASF; CI 346), is moderately fast to light and washing, and in spite of its being sensitive to mineral acid, it is used as a direct dye and chrome-printing color for cotton. The dye is more conveniently prepared by coupling diazotized *p*-nitroaniline with salicylic acid, reducing the nitro compound to the amine (III) by sodium sulfide, and condensing 2 moles of (III) with phosgene. The acid coupling of (II) with γ-acid gives Benzo Fast Pink 2BL (By; CI 353)

(II)





(III)



Benzo Fast Yellow 5GL

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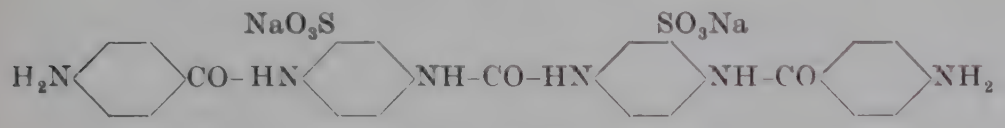
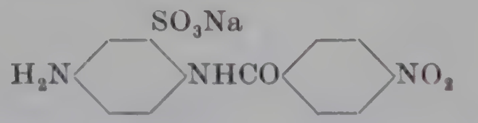
[23] See p. 494.

(Sirius Pink BB, IG)[5] which dyes cotton a bright pink with good fastness to light and washing. Benzo Fast Eosin BL (IG) (II $\rightrightarrows$ 2-methylaminonaphthalene-7-sulfonic acid, 2 moles) has good fastness to alkali, but poor fastness to light (3).[2] Brilliant Benzo Fast Violet 4BL, 5R (By; CI 353a) (γ-acid $\xleftarrow[\text{alk.}]{\text{acid}}$ II $\xrightarrow{\text{alk.}}$ phenyl-J-acid) has good fastness to light. Trypan Violet (I $\rightrightarrows$ H-acid, 2 moles) was used at one time against sleeping sickness, and is also of interest as a staining agent in the diagnosis of cancer.[12]

An interesting derivative of (II) is Diazo Light Yellow 2G (By; CI 654), which can be prepared in several ways, e.g., by phosgenating (IV), the condensation product of *p*-nitrobenzoyl chloride and *p*-phenylenediamine sulfonic acid, and then reducing. Although Diazo Light Yellow 2G is not a dye, it has good affinity for cotton, because of its linear symmetrical structure and the amide groups; by tetrazotization on the fiber and development with 1-phenyl-3-methyl-5-pyrazolone, a clear yellow shade with good all-round fastness is produced.



Diazo Light Yellow 2G



(IV)

Dyes from 4,4′-diaminodiphenylamine possess substantivity, but they are not technically important. Diphenyl Fast Black (Gy; CI 345) (γ-acid $\xleftarrow{\text{alk.}}$ 3,3′-dimethyl-4,4′-diaminodiphenylamine ⟶ *m*-toluylenediamine) has moderate fastness to light and washing, and is not sensitive to acids and alkalis. Trisazo and tetrakisazo dyes derived from diaminodiphenylamine are of practical value in the production of deep, fast blacks by aftertreatment with formaldehyde.[23]

Derivatives of 1,4- and 1,5-diaminonaphthalenes. Diamine Gold (C; CI 527), which is analogous to Chrysophenine G, is prepared by tetrazotizing 1,5-naphthylenediamine-3,7-disulfonic acid, coupling with 2 moles of phenol, and ethylating the two hydroxyl groups. It dyes cotton a pure yellow, stated to be fast to light, acid, alkali and chlorine and to be useful in printing for its easy dischargeability. Naphthylene Red (1,5-naphthylenediamine $\rightrightarrows$ naphthionic acid, 2 moles) is a red dye for cotton. Disazo dyes from 1,4-naphthylenediamine-2-sulfonic acid are acid dyes for wool and silk. These dyes are no longer employed commercially.

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[5] See p. 480.

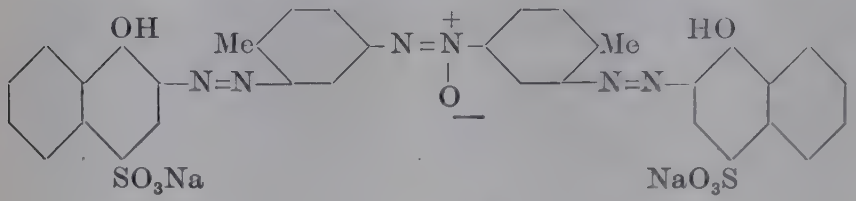
[12] See p. 489.

[2] See p. 480.

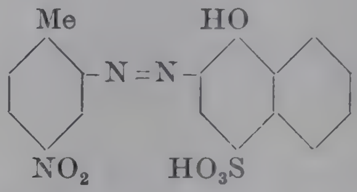
[23] See p. 494.

The 1,4-disazo derivatives of naphthalene which are important are the trisazo dyes prepared by the scheme ($A \longrightarrow M^1 \longrightarrow M^2 \longrightarrow E$), in which M^1 and/or M^2 are α-naphthylamine derivatives with a free 4-position.

Derivatives of 3,3′-diaminoazoxybenzene. A direct cotton dye, which is not derived from a *p*-diamine and the constitution of which is of considerable theoretical interest in view of its substantivity for cotton, is St. Denis Red (CI 604) prepared by coupling tetrazotized diaminoazoxytoluene with 2 moles of NW acid. The dye may be alternatively prepared by reducing the monoazo dye (V) in alkaline solution with glucose. It dyes cotton from a strongly alkaline bath containing a large quantity of salt a brilliant scarlet with low fastness to light and washing; it is also applicable to wool, the fastness on the protein fiber being better than on cotton. Replacing one mole of NW-acid in St. Denis Red by R-acid, the dye (Acid Milling Scarlet) is an acid color for wool, and has no affinity for cotton. The direct cotton dye Rosanthrene Bordeaux B has been stated to be (3,3′-diaminoazoxybenzene $\overset{\text{alk.}}{\underset{\longrightarrow}{\longrightarrow}}$ J-acid, 2 moles) (ST 332).

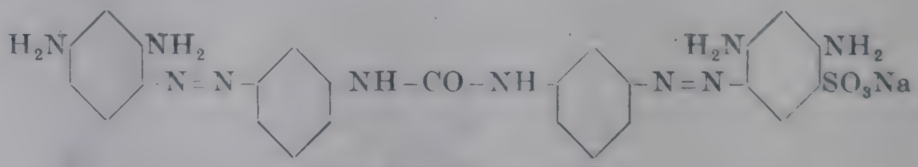


St. Denis Red



(V)

Derivatives of 3,3′-diaminodiphenylurea. Para Fast Brown GK (By; CI 352a) is substantive to cotton, but it is derived from *m*,*m*′-diaminodiphenylurea. *m*-Phenylenediamine (or *m*-aminophenol or a derived sulfonic acid) is the second component, and the dyes can therefore be developed on the fiber by coupling with a diazonium salt.[23]



Para Fast Brown GK

Dyes from diamines of heterocyclic compounds. Dyes of this type (e.g., Carbazole Yellow; Bohn, 1888; ST 531; 3,6-diaminocarbazole $\underset{\longrightarrow}{\longrightarrow}$ salicylic acid) are not of technical interest.

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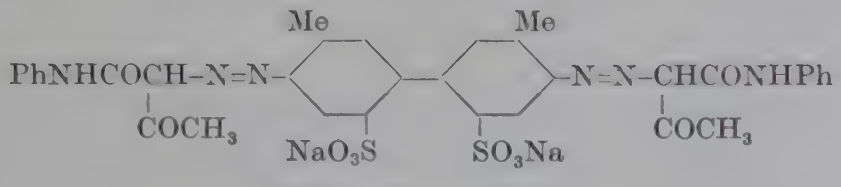
[23] See p. 494.

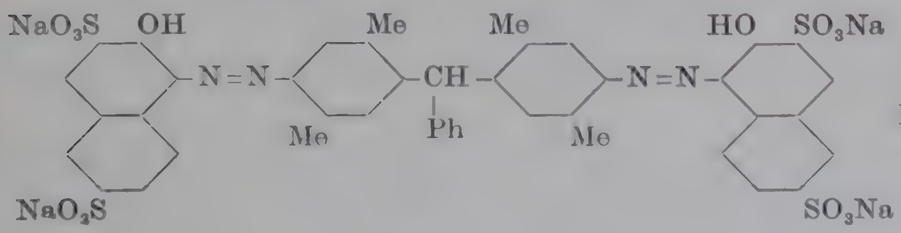
Acid Colors from Tetrazotized Diamines

While the dyes prepared by coupling certain diamines such as 2,2′-benzidine derivatives and diaminodiphenylmethane are devoid of affinity for the cotton fiber, they constitute a well-defined series of useful yellow to red acid colors, some of which are very fast to washing and milling. Milling Yellow H5G (IG) (*o*-tolidine-6,6′-disulfonic acid $\rightrightarrows$ acetoacetanilide,

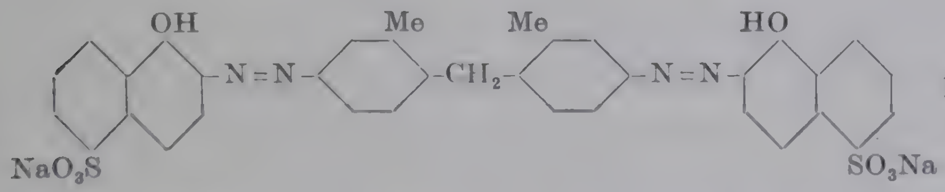


Milling Yellow H5G

2 moles) is a very greenish yellow with high washing fastness, as the name denotes, and moderate light fastness (5).[1, 4] Sulphon Yellow 5G (IG) is (benzidine-*m*-disulfonic acid $\rightrightarrows$ 2-methylindole, 2 moles). Acid Anthracene Red G (AGFA; CI 443) (benzidine-*m*-disulfonic acid $\rightrightarrows$ β-naphthol, 2 moles) is a yellowish red dye with low light fastness, but good fastness to milling. A more attractive and faster dye is Brilliant Carmine L (Hoffmann, 1887; BDC; CI 357) which is interesting because of the use of a diaminotriphenylmethane for tetrazotization and coupling; the dye was at one time used



Brilliant Carmine L



Milling Scarlet B

also for dyeing cotton and for the preparation of lakes. Fastness, both to light and milling, is further improved in Milling Scarlet B (MLB; CI 355).

m-Tolidine yields disazo acid dyes characterized by good milling fastness,[36] and several of the Supranol dyes (IG) are of this type.[2] Supranol Orange RR (G-acid ← *m*-tolidine → acetoacetanilide) has milling fastness (3–4), but only moderate light fastness (4) and leveling power (2–3). Supranol Scarlet G (acid GR ← *m*-tolidine → acetoacetanilide) and Supranol Red RX (acid GR ← *m*-tolidine → β-naphthol) have only moderate milling

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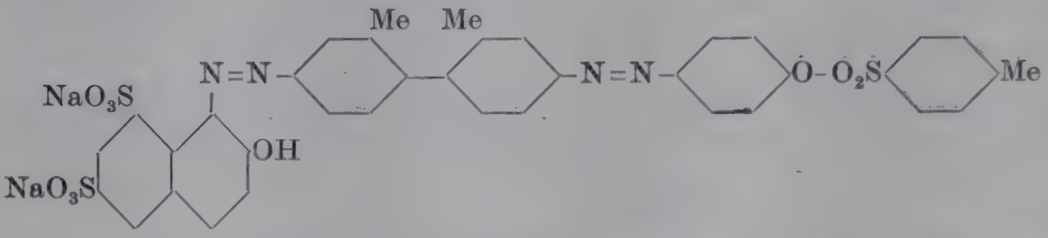
[1, 4] See p. 480.

[36] Kuhlmann, BP 481,477.

[2] See p. 480.

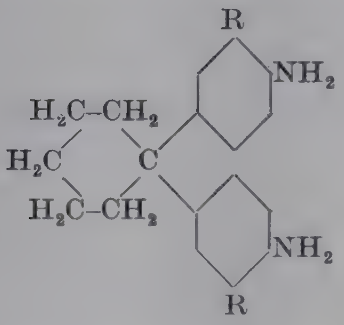
and light fastness (3 and 3–4).[2] Polar Orange GS (Gy) is prepared by the scheme (G-acid←—*m*-tolidine—→phenol; esterify with *p*-toluenesulfonyl chloride).[36a]



Polar Orange GS

In several commercial acid colors prepared from tetrazotized *m*-tolidine a 5-pyrazolone is used as one of the end components.[37] The 3,3′-dichloro-6,6′-disulfonic acid of *m*-tolidine has been used to prepare symmetrical and unsymmetrical disazo dyes with excellent fastness properties.[38]

A series of Supranol dyes with very good light fastness (5–7) and milling fastness (3–4) is made from the interesting diamines, 4,4′-diaminodiphenyl-1,1′-cyclohexane (I) and its derivatives (II) and (III). Supranol Orange GS and Scarlet FG are (G-acid←—I—→phenol and NW-acid, respectively).



(I; R=H)
(II; R=OMe)
(III; R=Me)

Supranol Red BR, Bordeaux B and Red BB are prepared by coupling two moles of 1,7-dihydroxynaphthalene-3-sulfonic acid with tetrazotized (I), (II) and (III) respectively. Treatment of the dye from (I) with benzenesulfonyl chloride gives Supranol Red BR.[2, 6]

Coupling benzidine or other diamine capable of yielding direct cotton dyes with certain second components, the products are acid colors; and if one of the second components is phenol or *m*-cresol, the phenolic hydroxyl may be esterified with *p*-toluenesulfonyl chloride, leading to members of the Polar (Gy) series, characterized by good fastness to light and excellent fastness to severe wet treatments. Polar Red G (Gy; CI 430) (G-acid←—benzidine—→phenol; esterify with *p*-toluenesulfonyl chloride); Polar Orange G (Gy),[36a] Supranol Scarlet GN (IG) (G-acid←—benzidine—→phenol;

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[2] See p. 480.

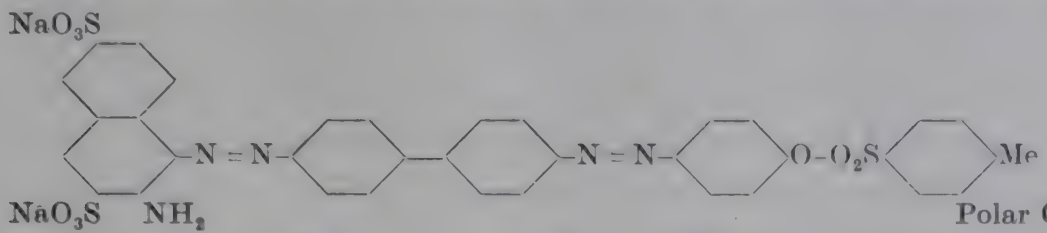
[36a] Rowe, The Development of the Chemistry of Commercial Dyes, Institute of Chemistry, London, 1938.

[37] See Chapter XVIII.

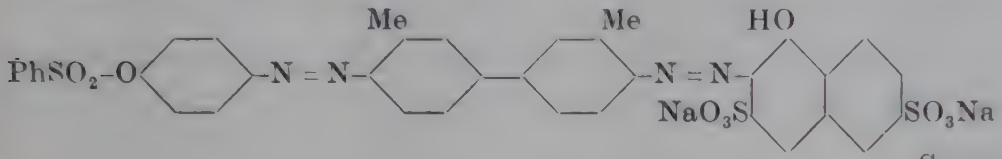
[38] Reynolds, Rossander, Kvalnes and du Pont, BP 569,080.

[6] See p. 480.

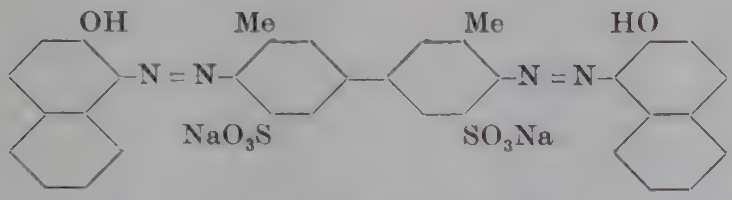
esterify with benzenesulfonyl chloride),[6] and Supranol Scarlet FGN (IG) are examples.[2] A dye which possesses at first sight the structural features of a direct cotton dye, but is used in fact as an acid and chrome mordant color for wool, is Acid Anthracene Red 3B (By; CI 487); however, it has been stated more recently that the dye is prepared from *o*-tolidine-6,6′-disulfonic acid.[2]



Polar Orange G



Supranol Scarlet FGN

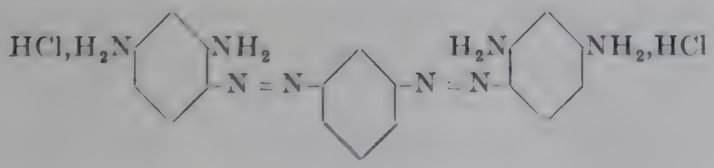


Acid Anthracene Red 3B

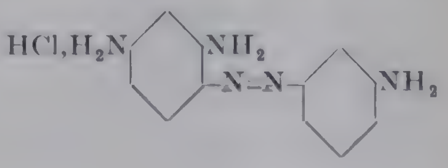
Octylphenols have been used as end components in the preparation of orange disazo dyes for wool and silk by the scheme (octylphenol←—benzidine disulfonic acid—→naphtholsulfonic acid).[39]

m-PHENYLENEDIAMINE DERIVATIVES

Basic dyes. Some of the oldest synthetic coloring matters belong to this very small group, and Bismarck Brown G (CI 331) was the first commercially important azo dye. When *m*-phenylenediamine is treated with an amount of nitrous acid insufficient for complete tetrazotization, the product, marketed as Bismarck Brown G, consists mainly of the disazo dye (I) together with a small amount of the monoazo dye (II). Bismarck Brown R (Griess, 1878; CI 332) is the analog from *m*-toluylenediamine. Both are basic dyes for cotton and leather, and are still largely used.



(I)



(II)

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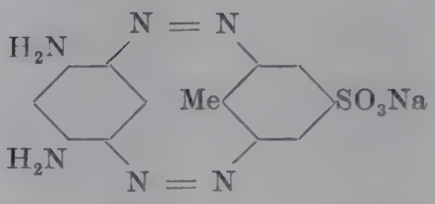
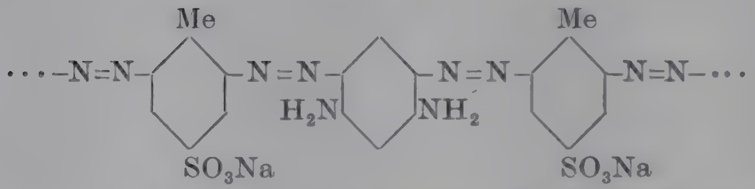
[6] See p. 480.

[2] See p. 480.

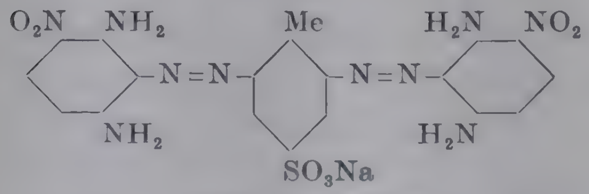
[39] Crossley, Shafer, and Calco, USP 2,127,478.

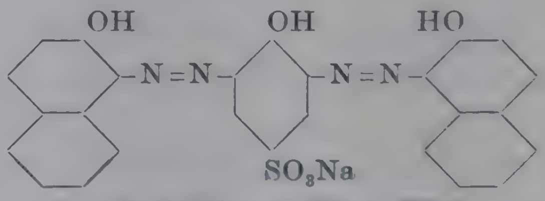
Acid and direct cotton dyes. 2,6-Diaminotoluene-4-sulfonic acid (III), on tetrazotization and coupling with one mole of *m*-phenylenediamine or two moles of other second components, yields direct cotton colors. The dyes are somewhat sensitive to alkali and have poor light fastness; for these and other reasons they do not appear to be represented in the current commercial range of cotton dyes. They are however of interest from the point of view of the relation between the chemical constitution of dyes and their affinity for cellulose. Toluylene Brown G (GrE) (CI 333) (III $\rightrightarrows$ *m*-phenylenediamine, one mole) dyes cotton direct a yellowish brown rendered much faster by developing on the fiber with diazotized *p*-nitroaniline. Ruggli and Fischer[40] have recently shown that the dye is not constituted as (IV), but has the chain structure (V), since diffusion experiments indicate that it is an ion-colloid.


(IV)


(V)

Coupling (III) with 4-nitro-*m*-phenylenediamine (2 moles) and β-naphthylamine (2 moles), Toluylene Yellow (GrE; CI 334) and Orange RR (GrE; CI 335) respectively are obtained. The acid-mordant color, Acid Alizarin Black SE (MLB; CI 336), is interesting for its method of preparation and the constitution of its metal complexes. When 2,6-diaminochlorobenzene-4-sulfonic acid is tetrazotized and coupled with two moles of β-naphthol, the chlorine atom is replaced by hydroxyl in the course of the reaction.


Toluylene Yellow


Acid Alizarin Black SE

BASIC AZO DYES

Apart from the old and well established azo dyes, Bismarck Brown and Chrysoidine, basic azo dyes containing quaternary ammonium groups have been prepared. Commercial examples are the Janus colors, which are now largely obsolete, but have a limited use for dyeing rayon (tannin-mordanting not being necessary) and for dyeing silk-wool union fabrics. The Janus colors can be applied to cellulose fibers by the usual tannin-tartar emetic process for basic colors; but because of their affinity they can also be dyed direct and then aftertreated with tannin or other fixing agents. While the shades have the poor light fastness characteristic of the basic dyes, they offer no advantage in cost, brightness or other factors over the triphenylmethane and heterocyclic basic dyes. The quaternary ammonium group may be present in the first component; or a diazonium salt may be coupled with a tertiary amine and the azo dye then converted into a quaternary ammonium salt. In the first method, a basic dye such as Safranine can be employed.

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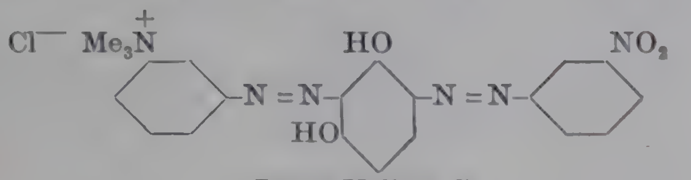
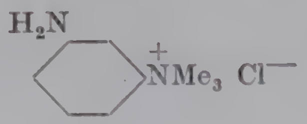
[40] *Helv. Chim. Acta* **28**, 445 (1945).

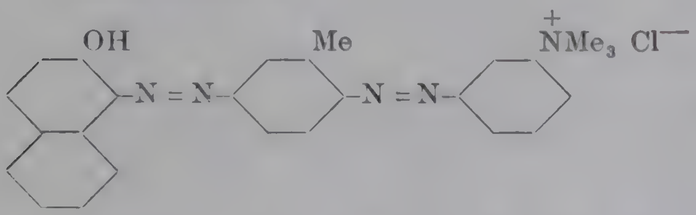
The yellow members of the series are primary disazo dyes from resorcinol. For Janus Yellow G (MLB; CI 236), the diazonium components are *m*-aminophenyltrimethylammonium chloride (I) and *m*-nitroaniline. Janus Red B (MLB; CI 266) belongs to the aminoazobenzene type of disazo dye (I⟶*m*-toluidine⟶β-naphthol). Janus Brown R (IG) (I⟶Chrysoidine Y)[5]



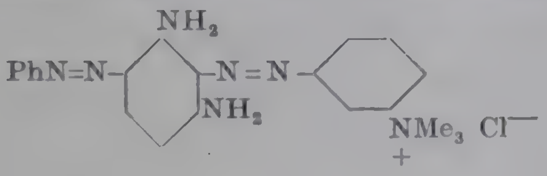
Janus Yellow G



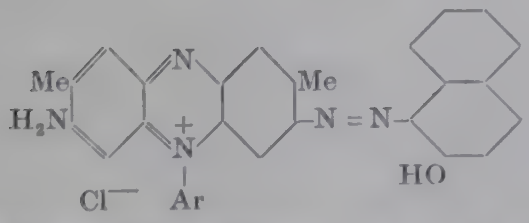
(I)



Janus Red B



Janus Brown R



Janus Blue G
($Ar = C_6H_5$ or $C_6H_4CH_3$)

is assigned a different constitution in CI 536 (*p*-aminobenzyldiethylamine ⟶α-naphthylamine⟶Chrysoidine Y), the latter being very similar to the constitution of Janus Brown B (MLB; CI 535) (I⟶α-naphthylamine⟶Chrysoidine). The first dyes of the series to have commercial success in dyeing and calico printing utilized Safranine as the diazonium component. In Janus Blue G (MLB; CI 135) (Indoine Blue R) the second component is β-naphthol; and an interesting feature of the dye is that, unlike the ordinary azo dyes which are decolorized by reducing agents, it gives a red Safranine dye on reduction, so that in discharge printing with stannous chloride red effects on a blue ground can be obtained. Replacement of β-naphthol in Janus Blue G by dimethylaniline gives Janus Green B (MLB; CI 133).

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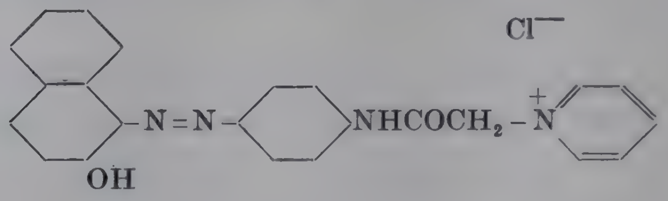
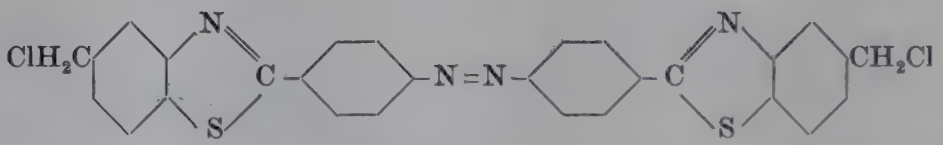
[5] See p. 480.

Basic azo dyes (e.g., II) may be produced by heating an azo dye, free from sulfonic groups, and containing a chloracetamido (-NHCOCH$_2$Cl) group with a tertiary amine such as pyridine or trimethylamine.[41] Basic dyes with substantivity for cotton, recently described, are the quaternary ammonium salts prepared by heating bis-chloromethyl-4,4′-dibenzthiazyl-(2)-azobenzene (III) with tertiary amines, such as pyridine, or tetramethylthiourea. Dyes of similar character have been mentioned in which the 5,5′-positions contain, in place of the quaternary ammonium groups, ternary sulfonium groups.[42] Cotton is dyed from a bath containing sodium carbonate or bicarbonate in yellow shades fast to washing, soda boiling and light.



(II)



(III)

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[41] Geigy, DRP 473,526.
[42] Haddock, Wood and ICI, BP 576,234; 576,270; USP 2,436,428; 2,439,804.

CHAPTER XIII

MORDANT AZO DYES

In the azo series there are two main classes of mordant dyes: (*a*) the azosalicylic acids, and (*b*) dyes in which one aryl residue carries a hydroxyl or amino group, and the second aryl residue a hydroxyl, amino or carboxyl group, both the substituents being *ortho* to the azo group. The technically important dyes of type (*b*) are mainly *o,o'*-dihydroxyazo compounds.[1-6]

o-Hydroxyazo and *o*-aminoazo dyes in general are liable to undergo oxidation by treatment with a dichromate, and to combine with chromium and copper with varying degrees of stability in the combination of metal and dye (or metal, dye, and fiber). Our present knowledge of the chemistry of such reactions and complexes is reviewed in the next chapter. As a matter of convenience in giving an account of the numerous azo dyes of varied types which are metallizable or possess mordant-dyeing properties, only two groups of dyes have been separately classified as "mordant azo dyes"; these are (*a*) dyes in which salicylic acid is the second or end component; and (*b*) dyes in which an *o*-aminophenol is the diazonium component, and in which the second component is so constituted that coupling takes place in the *o*- or adjacent position to a hydroxyl or amino group. Dyes of these two types are regarded as a distinct group, irrespective of the methods by which they are applied to textile fibers,[7] and of the fact that their metallization may involve oxidation prior to lake formation. All other azo dyes, which may have mordanting properties of one kind or another, have been included in the other groups of the azo dye classification, based on the number of the azo groups, the use of heterocyclic intermediates, and other structural features.

Among the many metals which can form coordination complexes, there are only two which are of interest in connection with azo dyes: chromium and copper. Chromium is outstanding, and in fact the nearly exclusive mordant for wool dyes, whether the metal-dye complexes are made on the fiber or in substance. Copper and chromium are both employed in conjunction with azo dyes for cotton, but copper is much more important. The azo chrome colors[8] are of the utmost technical importance in wool

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[1-6] As in Chapter XII.

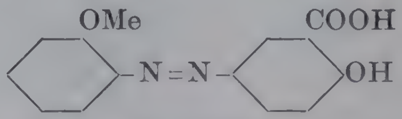
[7] See Chapter VI for an account of mordant dyeing and the onchrome, afterchrome, and metachrome processes.

[8] For a review, see Dorman, *Am. Dyestuff Reptr.* **32**, 47 (1943).

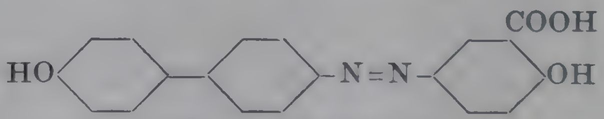
dyeing, and during the war they were widely used for dyeing military fabrics. Although tin and aluminium yield more brilliant shades, and copper and iron shades with greater light fastness, the use of chromium as a mordant leads to shades with good all-round fastness properties. Some of the chrome mordant dyes possess in fact the highest fastness to washing and severe wet treatments. The mordant azo dyes cover the entire color scale, but they are especially valuable for deep blues, violets, bordeaux, browns and blacks. The yellows are mainly reddish in tone, and the reds lack brightness; but in view of the fastness of the chrome dyes, research is continuously in progress to fill in these lacunae. Dyes applicable by the metachrome process and preformed metal complexes figure prominently in patents.

AZOSALICYLIC ACIDS

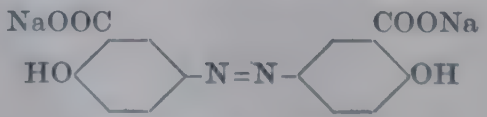
By coupling various diazonium salts with salicylic acid (I), yellow mordant dyes are formed, suitable for dyeing wool by one of the three chrome processes.[7] The azosalicylic acids are successors to the natural coloring matters, such as fustic in wool dyeing and Persian berries in calico printing, which they have completely replaced. An attractive feature of the azosalicylic acids is the brightness of the shades in contrast to most other mordant azo dyes. In their fastness properties which are good in general, a deficiency is fastness to potting. Alizarin Yellow R (Meldola, 1885; CI 40), GG (Nietzki, 1887; CI 36), 4G (AAP; CI 52) and 5G (Cb; CI 112), the last of which is a very greenish yellow, are useful dyes with good leveling and fastness properties. They are made by coupling (I) respectively with diazotized *p*- and *m*-nitroaniline, *p*-aminoacetanilide and *o*-anisidine. Glucose reduction of the dye (*p*-nitroaniline ⟶I) and sulfonation give Ergansoga Brown 3R (IG; ST II 102).[1] Diamond Flavine G (By; CI 110) is a useful dye, yielding a moderately fast yellow by all the three mordanting methods; the method of preparation is interesting: benzidine is tetrazotized, one diazonium group is coupled with a mole of (I), and the other diazonium group is replaced by hydroxyl by boiling with sulfuric acid. Eriochrome Flavine A (Gy; CI 219), which dyes a level greenish yellow as an acid color on wool and is changed to a



Alizarin Yellow 5G



Diamond Flavine G



Eriochrome Flavine A

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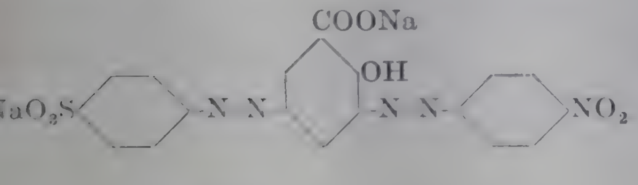
[7] See p. 523.

[1] See p. 523.

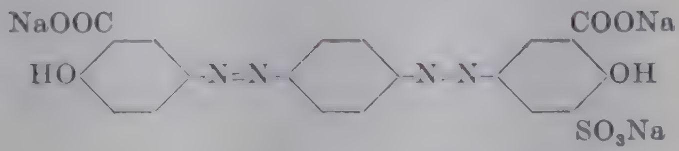
purer yellow with good fastness by afterchroming, also involves an interesting method of preparation; since both diazotized 5-aminosalicylic acid and (I) are sluggish couplers, the dye has to be made by coupling diazotized 2-chloro-5-aminobenzoic acid with (I) and then replacing the chlorine by hydroxyl by heating with caustic soda solution and copper. Other useful dyes of this type are Chrome Fast Yellow RR (IG) (2,5-dichloroaniline-4-sulfonic acid⟶I);[6] Eriochrome Phosphine R (Richard, 1909) (Gy; CI 157) (4-nitroaniline-2-sulfonic acid⟶I); and Metachrome Orange 3R (IG) (2-chloro-4-nitroaniline⟶I).[6] Naphthaleneazosalicylic acids are also employed, e.g., Mordant Yellow O (Nietzki, 1890; CI 195) (Brönner acid ⟶I); Mordant Yellow RL (IG) (naphthionic acid⟶I);[6] and Crumpsall Yellow (Lev; CI 197) (Alizarin Yellow CY, IG) (amido-G-acid⟶I).[2]

Among disazo mordant dyes there are several in which salicylic acid is employed. When one mole of a tetrazotized diamine is coupled with two moles of salicylic acid, the dyes are yellow. Chromocitronine R (DH; CI 441) (benzidine-2,2′-disulfonic acid$\rightrightarrows I_2$) and Anthracene Yellow C (C; CI 343) (4,4′-diaminodiphenylsulfide$\rightrightarrows I_2$) are also typical of symmetrically constituted azo dyes derived from 4,4′-diamines which have no affinity for cotton, but are useful as wool colors.[9] Chromocitronine R is a valuable chrome color in calico printing, the yellow shades having good washing fastness and excellent light fastness (7). Chrysamine G is a substantive dye for cotton. Chrome Yellow R (2-nitrobenzidine$\rightrightarrows I_2$) is useful for wool dyeing and for calico printing.[6]

Anthracene Acid Brown G (C; CI 238) is a dye in which (I) is used, like resorcinol or *m*-phenylenediamine, for dual coupling in the *o*- and *p*-positions (sulfanilic acid $\xrightarrow{1}$ I $\xleftarrow{2}$ *p*-nitroaniline); for the second and more difficult *o*-coupling, the more energetic diazonium salt of *p*-nitroaniline is employed.



Anthracene Acid Brown G



Azol Printing Orange R

Using (I) as one of the two phenolic components for coupling with a tetrazotized diamine, or as the end component for coupling with a diazotized aminoazobenzene or aminoazonaphthalene, a series of useful red, brown, bordeaux, and black wool dyes, some of which are also useful as chrome colors in calico printing, can be prepared. Milling Orange (MLB; CI 274)

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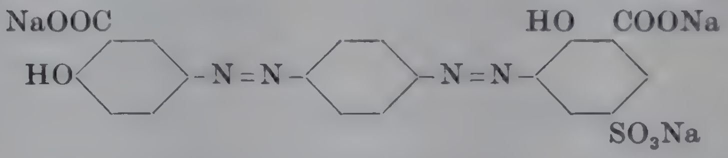
[6] See p. 523.

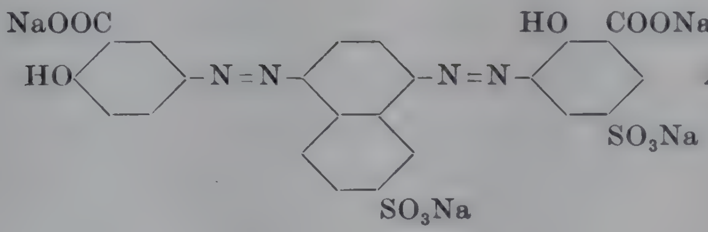
[2] See p. 523.

[9] See Chapter XII.

(Chrome Orange GR, IG), an aminoazobenzene type of disazo dye (sulfanilic acid⟶aniline⟶I), afterchromes to a fast orange red. Azol Printing Orange R (IG) contains two salicylic acid residues; *p*-nitroaniline is diazotized and coupled with (I); the nitro group is reduced by sodium sulfide and the amine is diazotized and coupled with (I); the disazo dye is finally sulfonated.[2] Ergansoga Orange R (IG) is prepared by condensing the monoazo dye (*p*-nitroaniline⟶I) with 3-aminosalicylic acid in presence of caustic soda solution, and sulfonating the disazo dye.[2] Azol Printing Brown 3RL (IG) also contains two salicylic acid residues and is prepared by the scheme (3-amino-5-sulfosalicylic acid⟶Cleve-6-acid⟶I). Anthracene Red (Gnehm and Schmid; 1892; CI 431) is (salicylic acid⟵2-nitrobenzidine⟶NW-acid). Alkaline condensation of 4-aminodiphenylamine-2-sulfonic acid with 5-*p*-nitrobenzeneazosalicylic acid gives a disazo dye which gives fast, bright brown chrome-prints on cotton.[10]

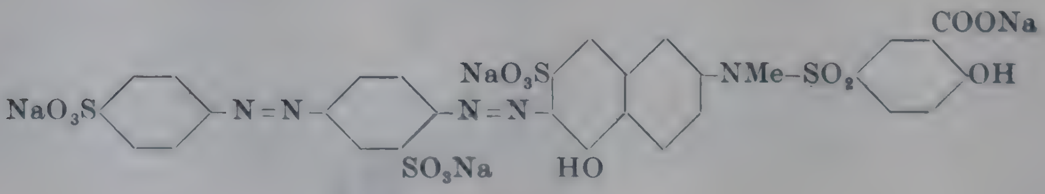


Ergansoga Orange R



Azol Printing Brown 3RL

In comparison with the *o*-hydroxyazo mordant dyes, the azosalicylic acids undergo only minor changes in shade by chroming—an advantage in matching shades and in the production of level dyeings. The alteration in color can be further minimized by separating the metallizing salicylic acid group from the chromophoric arylazo group by a sulfide, sulfone, sulfonamide, methylene, or similar insulating group. An example is Azol



Azol Printing Red R

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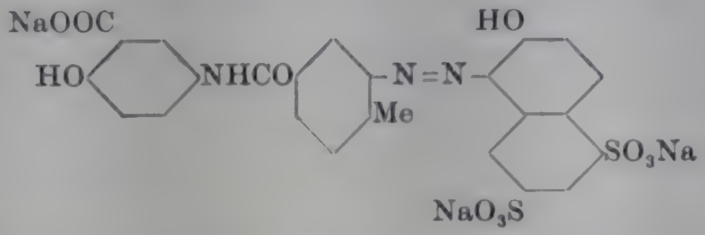
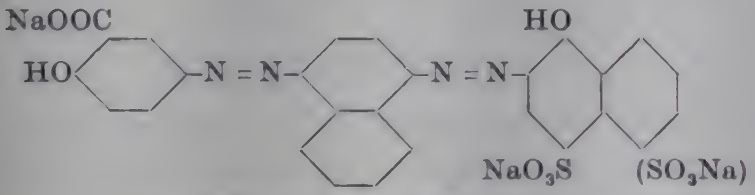
[2] See p. 523.

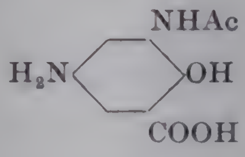
[10] Geigy, BP 595,491.

Printing Red R (IG).[2] The analog from γ-acid is Azol Printing Red 2B extra. Another example is Chrome Fast Orange RD (IG).[6]

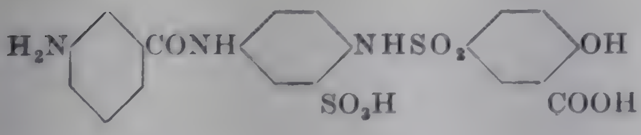

Chrome Fast Orange RD

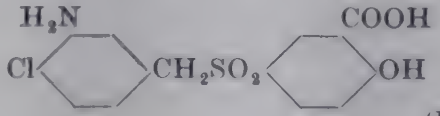
Azosalicylic acids may be prepared from the very slow-coupling diazotized 5-aminosalicylic acid (or the mixed 3- and 5-amino acids) as the first component. The important examples are disazo dyes, such as Diamond Black F (Lauch and Krekeler, 1889) (By; CI 299) (aminosalicylic acid⟶α-naphthylamine⟶NW-acid or α-naphthol-5-sulfonic acid), which gives a fast and beautiful black on wool by the afterchrome process, and Diamond Green B (By; CI 302) (aminosalicylic acid⟶1-naphthylamine⟶dioxy-S-acid), and Acid Chrome Black STC or STM (By; CI 303) (aminosalicylic acid⟶Cleve-7-acid⟶R-acid). An example of a monoazo dye is Diamond Bordeaux R (By) (3-amino-5-sulfosalicylic acid⟶NW-acid).[6] 5-Amino-3-acetamidosalicylic acid (II), prepared recently by acetylating 5-nitro-3-aminosalicylic acid and then reducing, yields brown dyes suitable for chrome printing on cellulosic fibers, when it is diazotized and coupled with β-naphthol-4-sulfonic acid.[11]


Diamond Black F


(II)

Because of the slow coupling of diazotized aminosalicylic acid and for other reasons, diazotizable amines in which the amino group and the salicylic acid residue are separated may be used with advantage. An example is (III), in which the carboxylamide and sulfonamide groups are


(III)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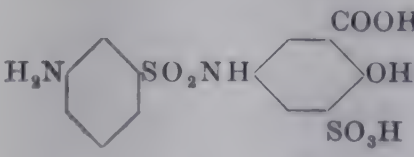
(V)

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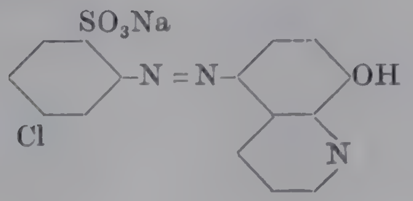
[2] See p. 523.

[6] See p. 523.

[11] Sandoz, BP 567,217.

likely to improve affinity and level dyeing.[12] Other intermediates for chromable dyes are the sulfone (IV) and the sulfonamide (V).

8-Hydroxyquinoline derivatives. Azo dyes from 8-hydroxyquinoline, e.g., Chrome Fast Orange G (IG),[1] resemble the azosalicylic acids in the nonparticipation of the azo group in the formation of the metal-dye complex. Metallizable disazo dyes, mainly bluish to yellowish red in color, obtained by coupling a diazotized aminoazo compound with 8-hydroxyquinoline, are applicable to cotton, rayon, wool, and leather.[13]



Chrome Fast Orange G

DYES FROM DIAZOTIZED *o*-AMINOPHENOLS

A series of important mordant dyes for wool are obtained by coupling diazotized *o*-aminophenol derivatives with various components. A single azo group is adequate for the production of dyes of practical value, although there are many disazo dyes in the series. As a class these dyes, which are applied mainly by the afterchrome process, have excellent fastness, particularly to wet treatments; but they are not without disadvantages. The shades, as might be anticipated from the nature of the dyeing process, are deficient in purity and brightness. The use of chlorinated intermediates is one method of improving the brightness. While the shades are orange to dark violet as direct dyes for wool, they are altered to brown, bordeaux, blue, dark green, and black by chroming.

o-Aminonaphthols are difficult to diazotize (see Chapter IV) owing to their tendency to be oxidized by nitrous acid to quinones. In special cases the hydroxyl group may be protected by acylation and the *O*-acyl group hydrolyzed after diazotization and coupling, but the normal procedure is to diazotize in presence of copper sulfate, or occasionally zinc chloride. Further, *o*-hydroxydiazonium salts (or diazo oxides) (see Chapter IV) do not couple very readily, and coupling is best carried out in a concentrated solution.

Some of the *o*-aminophenols employed are: 2-aminophenol-4-sulfonic acid (I) and its 6-nitro derivative (II; "black acid"); 4-nitro-2-aminophenol (III); 4-chloro-2-aminophenol (IV), its 5- and 6-nitro derivatives

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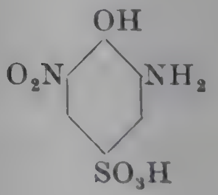
[12] Geigy, BP 470,037; IG, BP 471,125; Ciba, BP 517,642.

[13] Anderau and Ciba, USP 2,411,646; Ciba, SP 239,322-33.

[1] See p. 523.

(V and VII), and its 6-sulfonic acid (VI). These aminophenols undergo diazotization smoothly by the usual method.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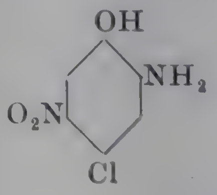
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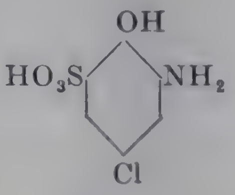
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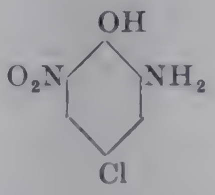
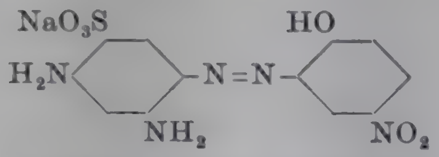
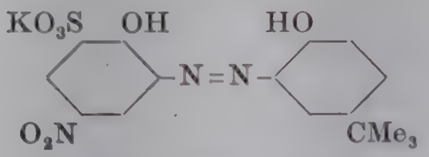

(VII)

Palatine Chrome Brown 2G (B; CI 98) (Acid Anthracene Brown RH, IG) (III—→*m*-phenylenediamine-4-sulfonic acid) dyes brown on chrome-mordanted wool. Acid Alizarin Brown B (Erdmann and Borgmann, 1893) (MLB; CI 167) (I—→*m*-phenylenediamine) is applied by the afterchrome process; the resorcinol analog, Acid Alizarin Garnet R (Erdmann and Borgmann, 1893) (MLB; CI 168), dyes brown, converted into bordeaux by afterchroming. All three have poor fastness properties, but are still employed. Acid Anthracene Brown LE (IG), applicable by a single bath process, yields faster shades;[1] the second component, *p*-*tert*-butylphenol, is important for the manufacture of varnish resins. Acid Anthracene Brown WSG (IG) is (II—→*p*-cresol).[5] Acid Alizarin Brown BB (MLB) (II—→*m*-phenylenediamine) and Anthracene Chrome Brown SWN (IG) (III→2,4-diaminophenyl ether of Schaeffer acid) have good fastness to light and milling. Acid Anthracene Brown M (III—→1-naphthol-5-sulfonic acid) and Acid Anthracene Brown R (picramic acid—→*m*-phenylenediamine-4-sulfonic acid; 33% converted into the glycine by condensation with chloroacetic acid) are other examples.[6, 14]


Palatine Chrome Brown 2G


Acid Anthracene Brown LE

A series of blue dyes are obtained by using α-naphtholsulfonic acids as the second component. Examples are Acid Chrome Blue 2R and 5R (IG) (VI—→1-naphthol-5-sulfonic acid and NW-acid respectively); Fast Mordant Blue B (IG) (IV—→chromotropic acid); Acid Chrome Blue 3G (IG) (V—→chromotropic acid).[2] Anthracene Chrome Blue R (C) is (4-acetamido-2-aminophenol-6-sulfonic acid—→β-naphthol).[6]

Palatine Chrome Violet (BASF; CI 169) (I—→β-Naphthol) dyes wool from an acid bath, a violet shade being obtained on afterchroming and a red (Copper Red N) (MLB; CI 169) by aftertreatment with copper sulfate.

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[1] See p. 523.

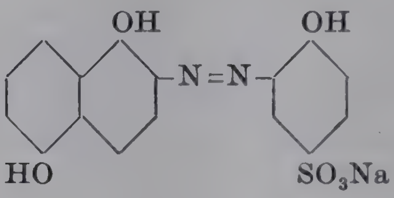
[5] See p. 523.

[6] See p. 523.

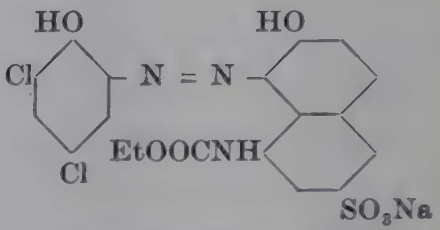
[14] See also Ciba, BP 588,165.

[2] See p. 523.

Acid Chrome Violet B (IG) (IV—→NW-acid) dyes wool a crimson shade, changed to violet by afterchroming. Acid Chrome Green G (6-chloro-4-nitro-2-aminophenol—→1,8-diaminonaphthalene-4-sulfonic acid; convert into a triazole) dyes wool dark violet, changed by afterchroming to a green with good fastness to light and milling.[6] Diamond Gray GL (IG), dyed by the afterchroming process, gives level shades with excellent fastness properties (light 6–7; milling 5; stoving 5).[3] Chrome Gray BN (IG) is (IV—→1,7-dihydroxynaphthalene-3-sulfonic acid), and Diamond Olive GL (IG) is (III—→1-phenylamino-7-naphthol-3-sulfonic acid).[1, 6] Using (I) with 1,5-dihydroxynaphthalene, coupling takes place in the 2-position,

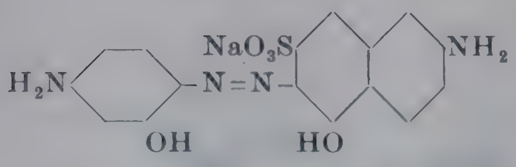


Diamond Black PV

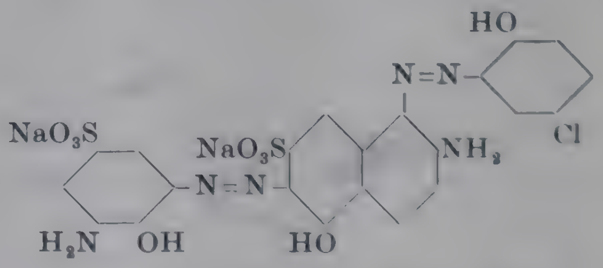


Diamond Gray GL

and the important dye, Diamond Black PV (Kahn, 1902; CI 170), which possesses very high all-round fastness and is outstanding in its fastness to potting, is obtained. It dyes wool red from an acid bath, converted into a fast black by afterchroming. Diamond Black PBB (IG) is (VI—→1,5-Dihydroxynaphthalene).[6] Diamond Blue Black BR (IG) is (VII—→phenyl-J-acid).[2] Acid Alizarin Black R (MLB; CI 172) (II—→β-naphthol) dyes by the afterchrome process a deep black very fast to light, but only moderately fast to washing. Autazol Chrome Black R (IG) (5-nitro-2-aminophenol $\xrightarrow{\text{alk.}}$ J-acid; reduce with sodium sulfide) is useful for dyeing wool and wool-staple fiber unions; the dark garnet shade from an ammonium sulfate-sodium sulfate bath develops to a fast black (light 6–7; milling 4–5) on treatment with Autazol Chrome Salt R and acetic acid. Autazol Chrome Black GR (IG) (IV $\xrightarrow{\text{acid}}$ J-acid $\xleftarrow{\text{alk.}}$ II; then reduce nitro to amino) is a green supplement to the R brand.[3]



Autazol Chrome Black R



Autazol Chrome Black GR

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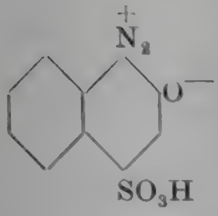
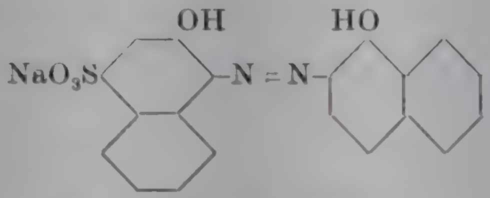
[6] See p. 523. [3] See p. 523. [1] See p. 523. [2] See p. 523.

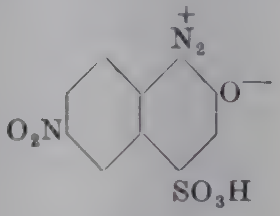
An important diazonium component for a series of largely used mordant dyes for grays, blue-blacks and blacks with excellent all-round fastness is 1-diazo-2-naphthol-4-sulfonic acid (VIII). Salicine Black RLF (IG) is (VIII—→resorcinol).[6] Coupling with α-naphthol is mainly in the 2-position; the product, Eriochrome Blue Black B (Salicine Blue Black AE)[6]



(VIII)

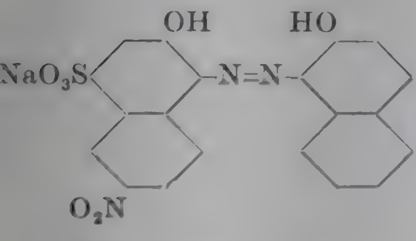


Eriochrome Blue Black B

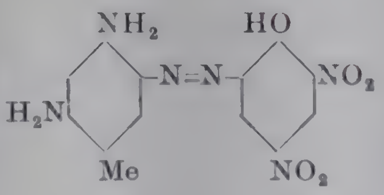


(IX)

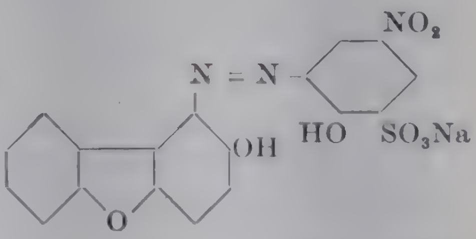
(Gy; CI 201) and the analog from β-naphthol, Eriochrome Blue Black R (Gy; CI 202), are major products in the range of azo mordant colors. Nitration of (VIII) gives the 6-nitro compound (IX) which couples with α-naphthol exclusively in the 2-position and another valuable dye, Eriochrome Black T (Gy; CI 203) (Chromogen Black ET, IG),[6] is obtained. The reddish-black shade on wool from an acid bath afterchromes to a very fast bluish-black. The β-naphthol analog is Eriochrome Black A (Gy; CI 204) (Chromogen Black EA, IG)[5] which dyes wool a dark red-brown as an acid color, afterchromed to a deep fast black with excellent fastness to light, but only moderate fastness to milling; special precautions have to be taken in the dyeing process to obtain level shades. When the dye is converted into a chromium complex, mixed with half a mole of the unchromed dye, the nitro group reduced by means of sodium sulfide, and the amine condensed with *p*-toluenesulfonyl chloride, the product is Silk Fast Gray BB (IG).[5] Diamond Green 3G (IG) has been stated to be (4-nitro-2-amino-1-naphthol—→H-acid; contrast CI 302).[5]



Eriochrome Black A



Metachrome Brown B



Acid Anthracene Brown TBL

Mordant dyeing has been made simpler by the preparation of dyes which can be applied to fibers simultaneously with the mordant in a single bath. The usual procedure, called the metachrome (or monochrome or chromate) process, employs as the mordant a mixture of ammonium sulfate and sodium dichromate. The first component for preparing many of the dyes in this series is picramic acid. Dyes from picramic acid are explosive, and are best stored as aqueous pastes or in high dilution with Glauber salt. Some of the brown and olive dyes contain one hydroxyl and one amino group *ortho* to the azo group, and examples are Metachrome Brown B (AGFA; CI 101) and Chrome Olive 2B (By; CI 102) (picramic acid ⟶ β-naphthylamine). While Metachrome Olive Brown G (AGFA; CI 104) (picramic acid ⟶ *p*-cresol) yields an olive-brown shade as a metachrome or afterchrome color, the replacement of *p*-cresol by *m*-4-xylenol leads to an olive-green shade.[15] Acid Anthracene Brown TBL (IG) may be applied by the afterchrome or metachrome method, and possesses good solubility, leveling property and excellent fastness (light 6–7; other agencies 4–5).[3] The range now includes all colors. A series of important mordant dyes are prepared from pyrazolone derivatives as coupling components and among them are two Metachrome Reds.[16] By introducing chlorine atoms and nitro groups in the diazonium component, and using a naphthol as the second component, bordeauxs, blues and blacks become available. Metachrome Bordeaux R (AGFA; CI 107), Brilliant Blue 8RL (3,4,5-trichloro-2-aminophenol ⟶ NW-acid), Green 2B (III ⟶ 1,8-diaminonaphthalene-4-sulfonic acid; convert into a triazole),[6] Blue Black 2BX (VII ⟶ Schaeffer acid), Blue Black PBX (VII ⟶ 1-naphthol-5-sulfonic acid), and Black Blue G are among the present members of the Metachrome (IG) series.[17] A disazo Metachrome dye is Metachrome Brown BC (III ⟶ *m*-phenylenediamine ⟵ Laurent acid). Metachrome Brown EB is prepared from the same components, but the method of isolation of the dye is modified and the product is shaded with 2% of Alizarin Blue Black B; a by-product, isolated from the filtrate, is marketed as an acid dye, Alphanol Brown R (IG).[2] The monochrome dyes (IG) are similar to the Metachrome dyes. An example is Monochrome Blue R (VI ⟶ β-naphthol).[5]

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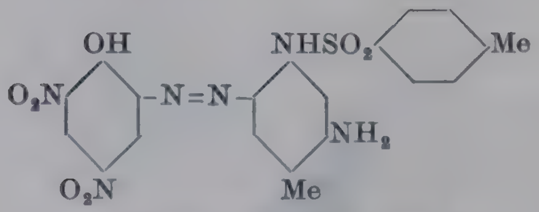
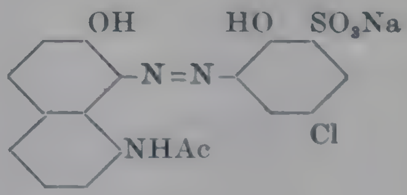
[6] See p. 523.

[5] See p. 523.

In preparing disazo mordant dyes with an *o,o'*-dihydroxyazo grouping, an *o*-aminophenol derivative may be used as the middle component. An example is Eriochrome Verdone A (Gy; CI 292) (sulfanilic acid ⟶ 3-amino-*p*-cresol ⟶ β-naphthol), which dyes bordeaux-red as an acid color,



Metachrome Bordeaux R



Metachrome Black Blue G

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[15] Brotherton and Co., BP 563,772.

[16] See Chapter XVIII.

[17] *BIOS* 271.

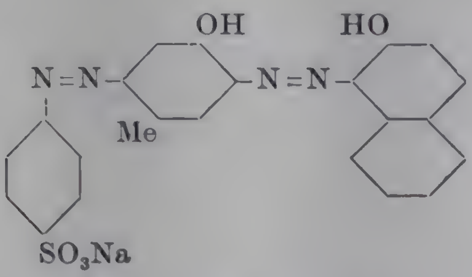
[2] See p. 523.

[3] See p. 523.

[6] See p. 523.

[5] See p. 523.

afterchromed to a fast bluish-green. Replacing sulfanilic acid by 4-chloroaniline-3-sulfonic acid, the product is Acid Alizarin Blue Green L (IG).[2] 3-Amino-*p*-cresol couples slowly and the diazonium salt is therefore stabilized by the addition of sodium thiosulfate or sodium naphthalene-β-sulfonate. The use of an *N*-arylsulfonic acid as the end component is claimed to give a faster green.[18]



Eriochrome Verdone A

Yellow to brown dyes are obtained by coupling *o*-aminophenol and its derivatives with *peri*-naphthindandiones; the dyes may be chromed on the fiber or converted into chromium complexes in substance.[19] A nuclear alkyl substituent (e.g., C_5H_{11}) may be present in the *o*-aminophenol derivative to be diazotized and used in the preparation of chrome colors.[20] The dyes (XII⟶phenol with *tert*-alkyl C_{4-8} in the 2-position and alkyl C_{1-8} in the 4-position) are applicable by the metachrome process and the olive-brown shades have good fastness to potting.[21] The alkoxyresorcinol (X; $R = C_8$ to C_{15}, preferably $C_{11}H_{23}$), on coupling with one or two moles of a diazonium salt, gives acid colors for wool, silk and leather; if the diazonium salt is an *o*-aminophenol derivative, the dyes can be used as chrome colors. Monoalkyl (C_8–C_{15}) ethers of phloroglucinol can also be used.[22]

Bluish green azo dyes prepared by coupling diazotized (XII) with *N*,*N*′-dialkyl- or *N*,*N*,*N*′,*N*′-tetraalkyl-1-amino-8-naphthol-3,6-disulfonamide, applied by the metachrome or afterchrome process, exhaust better and give brighter shades than previously reported dyes.[22a] The disazo dye (III⟶S-acid⟶2-methoxyacetoacetanilide) gives a green shade of good fastness on chroming.[22b] Green dyes (e.g., XI) suitable for the afterchrome process, in the preparation of which the first component has a sulfonamide group and the second component is 2-amino-3-naphthoic acid, have been described.[23] Green chrome dyes, which are fast and level dyeing, are also obtained by coupling diazotized *o*-aminophenols with 2-amino-3-carboxynaphthalenesulfonic acid. The dye (4-*m*-sulfobenzoyl-2-aminophenol ⟶ 2-amino-3-naphthoic acid) gives a yellow-green shade by afterchroming.[24] The gray-blue shades from the dye (VII ⟶ 2-naphthol-4-sulfon-*N*-carboxymethylamide) by the metachrome method have outstanding light fastness.[25] The dyes (4-chloro- or 3,4-dichloro-5-nitro-2-aminophenol-6-sulfonic acid ⟶ 5,8-dichloro-1-naphthol) dye blue to blue-gray by the metachrome method.[26] The dye (XII ⟶ 6-bromo-2-naphthol) gives fast black shades by the metachrome process.[27] The dye (IX ⟶ 5-chloro-1-naphthol), by the afterchrome process, dyes wool a black of excellent fastness to light, fulling and potting.[27a] The monoazo dye (XII ⟶ 1-phthaloylimido-7-naphthol) dyes a bright green by the metachrome process, but an olive black by the afterchrome process.[27b]

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[2] See p. 523.

[18] Geigy, BP 510,058.

[19] Ciba, BP 509,360; 515,098; 516,425.

[20] Geigy, BP 561,228; SP 233,353-8.

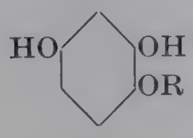
[21] Geigy, BP 576,306; SP 231,414-21.

[22] du Pont, BP 512,839.

[22a] Beech, Mendoza, and ICI, BP 615,606.

[22b] Anderson and Allied Chemical and Dyestuff, USP 2,474,024.

[23] Geigy, BP 544,887. For examples of dyes containing sulfonamide groups and no sulfonic groups, see Conrad, USP 2,499,133; Ciba, BP 630,452.



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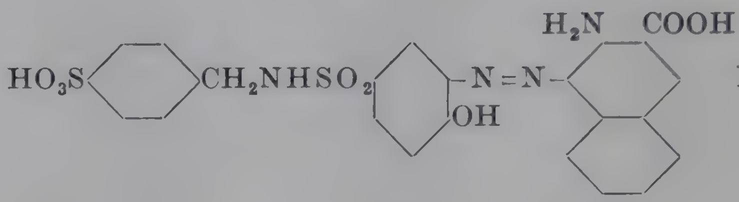

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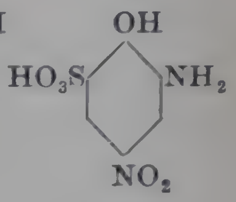

(XII)

SOLUBLE CHROMIUM COMPLEXES OF MORDANT AZO DYES

An example of the success of the color chemist in simplifying the work of the dyer is the group of Neolan and Palatine Fast colors. The principle of preparing soluble metal complexes of mordant dyes was discovered by Bohn in 1912; these were the Ergan dyes (BASF)[28] which were soluble chromium complexes of the azosalicylic acids, recommended for calico printing. Improvements in the method of preparation and the development of procedures by which such metal complexes could be applied to wool and silk from an acid bath enabled Ciba to market a wide range of "Neolan" colors (from the Greek "neo-lana"—new wool), derived from dyes other than the azosalicylic acids. The Palatine Fast dyes of the IG are similarly constituted. The Neolans and Palatine Fasts, of which there are now about fifty of all shades from yellow to black, are notable for the fact that they dye like ordinary acid dyes, except for the larger proportion of acid necessary, but are much faster for the reason that they are chrome dyes. The comparatively high concentration of sulfuric acid employed converts the water-soluble chromium complex into an insoluble fiber-metal-dye complex. Dyed under suitable conditions, the Neolans and Palatine Fasts yield level shades of excellent fastness. In comparison with the shades obtained by the usual chrome dyeing methods, the light and other fastness properties of the Neolans are approximately the same, but the fastness to severe washing (e.g., to potting or heavy milling of deep shades) is somewhat inferior. Matching shades is easier with the Neolans, which are comparable with the acid colors from this point of view, since they are dyed by a single-stage direct process. Dyeing with a preformed chromium complex of a dye is not equivalent to the production of the complex on the fiber by mordanting and dyeing in whatever order the two processes may be carried out. The difference is not merely in the chemical constitution of the fiber-dye-metal complex which is ultimately produced by either method; usually the shade obtained from the soluble metal complex is brighter than the shade obtained by mordant dyeing, and frequently the latter has the advantage in fastness. While the original *o*-hydroxyazo dye is very sensitive to copper and other metals, and therefore limits the choice of materials of construction for wool dyeing equipment, the " metallized " dye is no longer affected by metals.

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[24] Geigy, BP 586,597.

[25] Geigy, SP 219,933. See also SP 222,997-8.

[26] Geigy, USP 2,447,164.

[27] Mendoza and ICI, USP 2,436,013.

[27a] Ciba, SP 243,966.

[27b] Grimmel, Richter and General Aniline and Film, BP 632,092.

[28] Rowe, The Development of the Chemistry of Commercial Dyes, Institute of Chemistry, London, 1938, p. 29.

The stability of some of the preformed chromium complexes is indicated by a patent,[29] which claims the removal of a sulfonic group from a chromium complex by heating in an autoclave with sulfuric acid. The azo dye (2-amino-1-naphthol-4,8-disulfonic acid ⟶ β-naphthol) is converted into a chromium complex by heating with chromic oxide, formic acid, and water. On heating the complex with sulfuric acid in an autoclave, the 4-sulfonic group is split off, and the monosulfonic acid dyes wool in fast blue shades. Metallized dyes containing nitro groups may be reduced to the amines, and the amino groups then submitted to such reactions as benzoylation and phosgenation, the coordinated metal remaining intact throughout. It has been claimed that metalized dyes may be thionated without decomposition of the metal chelate groups, but this is very unlikely and the sulfurized dye may merely contain the metal in an insoluble form. The azo groups in both the parent azo dyes and the metal complexes undergo reductive fission by sulfurization.

Copper and chromium complexes appear to have been used at one time, but the present series of Neolans and Palatine Fasts consist exclusively of chromium complexes. A few copper complexes (Lanasol dyes, Cb) were introduced in 1924, but they are apparently no longer marketed. Lanasol Violet R (ST 243) was the copper complex of Chrome Fast Black

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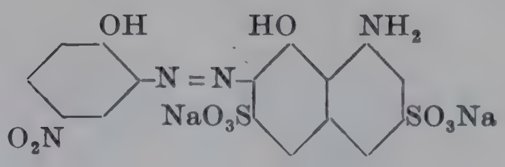
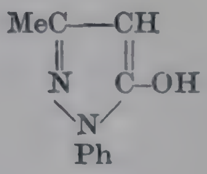
[29] IG, DRP 651,429.

PW (Cb; CI 202) (VIII⟶β-naphthol). Peri Wool Blue B "F" (IG) (cf. CI 100) is stated to be the copper complex of (III⟶Chicago acid).[6] Copper complexes applicable to wool and silk have been described in recent patents. For instance, copper complexes of disazo dyes from resorcinol, in which one of the diazonium components is an *o*-aminophenolsulfonic acid, are brown dyes for wool and silk, fast to light.[30] Copper complexes are useful as leather dyes. In recent years copper complexes applicable to cotton as direct dyes have been extensively developed. Although the commercial metal-azo dye complexes appear invariably to utilize chromium for wool dyes and copper for cotton dyes, the patent literature mentions various other metals such as manganese, iron, cobalt, nickel, vanadium, tungsten, molybdenum, tellurium, zirconium and titanium.

While some of the chromium complexes are prepared from new azo dyes, several are derived from old and well-known acid mordant colors. Thus Neolan Red B is the chromium complex prepared from Eriochrome Red B[16] and Neolan Blue B from Eriochrome Blue Black R (see Tables I and II). When an aqueous solution of Eriochrome Green H (Gy; CI 99) is boiled with chromium fluoride and salted out, a green chromium complex is obtained (Ciba, 1915), which dyes a faster and better green than the original acid dye by the afterchrome process.



Eriochrome Green H



(XIII)

The chromium complexes may be prepared by two methods, of which the first is much more important: (*a*) treatment of the azo dye with a chromium salt (formate, acetate, fluoride, sulfate); and (*b*) coupling a diazotized *o*-aminophenol or -naphthol derivative with a suitable second component in presence of a chromium salt, so that the coupling and metallization take place simultaneously. In either case the coupling components are such that the azo dye contains two hydroxyl groups *ortho* to the azo group; while the *o,o′*-dihydroxyazo dyes represent the general type, the second *o*-position may be occupied by an amino or carboxyl group. The common first components are (II), (VI), (VIII), (IX) and 4-nitro-2-aminophenol-6-sulfonic acid (XII); the common second components are α-naphthol and its 4- and 8-sulfonic acids, β-naphthol, phenylmethylpyrazolone (XIII), and acetoacetanilide.

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[6] See p. 523.

[30] Geigy, BP 577,673.

[16] See p. 532.

The typical procedure for the preparation of chromium complexes is to heat the dye in aqueous solution with a chromium salt under conditions such as the following, and salt out the complex: (*a*) for 12-24 hours with chromium sulfate; (*b*) with alkaline solutions of chromium salts (e.g., sodium chromite) in presence of polyhydroxy compounds such as sugar or glycerin; (*c*) with a chromium salt under pressure in an autoclave. Recently described chroming agents are ammonium-chromium salicylate and sulfosalicylate; the complex is formed by agitating an aqueous solution of the azo dye and the reagent at 90–100° for about two hours.[31] The azo dye and the metal salt may be heated at 80–150° in the molten, hydrated alkali salt of formic, acetic or chloroacetic acid.[31a] The main IG method of manufacture of Palatine Fast colors is to heat the aqueous solution of the azo dye with chromium formate (or occasionally chromium sulfate) at 115° (in special cases 135°) in a steel autoclave, rubber-lined and further tiled with porcelain tiles; the complex is separated by cooling, and if necessary by adding salt or hydrochloric acid or both. Chromium formate is used in the form of a freshly prepared solution of chromium oxide in technical formic acid. In its final form the chromium complex can contain free sulfonic groups, or is converted into the sodium salt by heating with caustic soda solution. Control of pH is a vital factor, and while the reaction is mainly carried out at the boil, lower temperatures are suitable for some dyes. The time of treatment merely depends on the completion of the metallization, which may be determined by a dye-trial or by absorption spectra measurements; the properties of the dye will not undergo further alteration when the metal-dye reaction has been completed. The commercial dyes may be mixtures of chromed and unchromed dyestuffs, and may in addition contain basic chromium salts.[1]

It is sometimes preferable to protect the hydroxyl group in an *o*-aminophenol (e.g., by tosylation) before diazotization and coupling. When 3-amino-4-tosyloxybenzenesulfonamide is diazotized and coupled with G-acid, the tosyl group saponified, and the *o*-hydroxyazo dye converted into a chromium complex by prolonged boiling with chromium sulfate, a bordeaux dye with good leveling power is obtained.[32]

The constitution of the acid colors of which the Neolans are chromium complexes is known in a few cases (Table I).[33] The constitution of the azo dyes from which the Palatine Fast dyes are made is stated in Table II.[1]

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[31] Geigy, BP 560,787; 591,454; USP 2,417,735; 2,428,866.

[31a] Sandoz, SP 241,415.

[1] See p. 523.

[32] Ciba, BP 512,939.

[33] Fierz-David, Künstliche Organische Farbstoffe, Ergängzungsband. Springer, Berlin, 1935.

TABLE I

AZO DYES CORRESPONDING TO THE NEOLANS

Neolan	*Azo dyes*	
	Name	*Constitution*
Yellow GR		(XII)→Acetoacetanilide
Red R		(VI)→(XIII)
Red B	Eriochrome Red B	(VIII)→(XIII)
Blue B	Eriochrome Blue Black R	(VIII)→β-Naphthol
Blue G		(VIII)→α-Naphthol
Blue 2G		(VIII)→1-Naphthol-8-sulfonic acid

TABLE II

AZO DYES CORRESPONDING TO THE PALATINE FAST COLORS

Palatine Fast	*Azo dye*
Yellow ELN	4-Sulfoanthranilic acid→(2′-Methyl-4′-sulfo–XIII)
Yellow 3GN[5]	Metanilic acid→Salicylic acid
Yellow 6GEN	3-(*m*-Amino)benzenesulfonamido-5-sulfosalicylic acid→3-Methyl-5-pyrazolone
Yellow GRN	(XII)→Acetoacetanilide
Yellow RX	2-Naphthylamine-5/8-sulfonic acid→*p*-Cresol (90)+*o*-Cresol (10)[6]
Orange GN (GEN)	(XII)→(XIII)
Orange RN	(II)→(XIII)
Red BEN	(II)→2,4-Dihydroxyquinoline
Red GREN	(VI)→(*m*-Sulfo-XIII)
Red LEN	6-Nitro-4-methyl-2-aminophenol→(*o*-Sulfo-XIII)
Red RN	(VI)→(XIII) (Mixture of 2 moles chromed and 1 mole unchromed dye)
Rose BN	(VIII)→(*m*-Sulfo-XIII)
Violet 3RN	4-Chloro-*o*-anisidine→Schaeffer acid (Demethylation occurs during chroming)
Violet 5RN	4-Chloro-*o*-anisidine→G-acid
Bordeaux RN	(VI)→2,4-Dihydroxyquinoline
Bordeaux BN	*o*-Anisidine-4-sulfondiethylamide→G-acid (Demethylation during chroming)
Marine Blue RENA	Mixture of Blue GGN, Violet 3RN, Rose BN and Patent Blue AF
Blue BN	(VIII)→β-Naphthol
Blue GGN	(VIII)→1-Naphthol-8-sulfonic acid
Blue 3959 (for mixing with GGN to give Blue RRN)	4-Chloro-*o*-anisidine→ε-acid (Demethylation during chroming)
Dark Blue GN	4-Chloro-5-nitro-*o*-anisidine→1-Naphthol-4,8-disulfonic acid (Demethylation and partial splitting off of sulfonic group during chroming)

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[5] See p. 523.

[6] See p. 523.

TABLE II (*continued*)

Palatine Fast	*Azo dye*
Blue Black BN	(IV)—→2,8-Dihydroxynaphthalene-6-sulfonic acid[5]
Green BGN	(II)—→β-Naphthylamine
Green BLN	5-Nitro-2-aminophenol—→2-Naphthylamine-5-sulfonic acid
Dark Green BN	Picramic acid—→Naphthionic acid
Brown BRRN	(XII)—→β-Naphthol
Brown RN	(XII)—→*p-tert*-Butylphenol
Brown TCN (TNC)	Picramic acid—→*m*-Phenylenediamine-4-sulfonic acid (Mixture of 2 parts of chromed and 1 part of unchromed dye)
Black WAN	(IX)—→β-Naphthol (Mixture of chromed and unchromed dye)
Black GGN	(IX)—→1-Naphthol-8-sulfonic acid[5]
Black RRN (Wool Black N)[6]	(II)—→β-Naphthol[5]

Application of soluble chromium complexes. For wool, the dyebath contains 10% Glauber salt and 6–8% of concentrated sulfuric acid on the weight of wool.[7] The two important factors of acid strength and time of boiling have to be varied within certain limits for each dye. These chromium complexes are remarkably stable to prolonged boiling with mineral acid, although some (like Neolan Yellow R) are more readily affected than the others; but all the metal-complexes are sensitive to polycarboxylic acids such as oxalic, citric and tartaric acids.

Applied to slubbing, the chromium complexes affect the spinning properties of the fiber less than the ordinary chrome dyes. For classes of wool liable to damage by excessive acid treatment, dye manufacturers have introduced auxiliary agents (e.g., " N Salt NS II " of Ciba), by using which the sulfuric acid content of the dyebath may be reduced.[33a] If 5–7% of Dispersol A (ICI) is used in the dyebath in dyeing the Neolans, the quantity of sulfuric acid necessary can be cut down by half. Demetallization of premetallized azo dyes containing *o*-amino groups during dyeing, and harshness and tendering of wool, are prevented by the presence of aldehydes.[34]

The Zapon Fast colors (IG) are chromium complexes of azo dyes, similar to the Palatine Fast dyes, but with the difference that they are recommended for the coloration of lacquers. They are prepared by first separating the azo dye and chroming with chromium formate or chromium fluoride. Table III gives the constitution of the azo dyes from which some of the Zapon Fast dyes are made.[5]

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[5] See p. 523.

[6] See p. 523.

[7] See p. 523.

[33a] See also Millson, Mooradian and American Cyanamid, USP 2,470,080.

[34] Royer and Amick, USP 2,422,586.

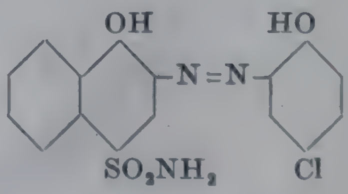
TABLE III

AZO DYES CORRESPONDING TO THE ZAPON FAST DYES

Zapon Fast	*Azo dye*
Yellow GR	(XII)⟶Acetoacetanilide
Yellow R	Anthranilic acid⟶(XIII)
Orange G (Same as Palatine Fast Orange GN)	(XII)⟶(XIII)
Orange RR (Same as Palatine Fast Red RN)	(VI)⟶(XIII)
Red BE	5-Nitro-2-aminophenol⟶(XIII)
Red GE	(III)+Anthranilic acid⟶(XIII)
Violet BE (Cobalt complex)	5-Nitro-2-aminophenol⟶β-Naphthol
Violet R	(VI)⟶β-Naphthol
Blue G (Chromium complex, acid form)	(VIII)⟶α-Naphthol
Black NCB	4,6-Dinitro-2-aminophenol⟶2-Naphthol-4-sulfonic acid (the chromium compound is converted into the isopentadecylamine salt)
Black NC	4,6-Dinitro-2-aminophenol⟶β-Tetralol
Black PF	5-Nitro-2-aminophenol⟶β-Naphthol
New Black	5-Nitro-2-aminophenol⟶β-Naphthol (1 atom chromium to 2 moles dye)

NEUTRAL DYEING METAL COMPLEXES

Neutral dyeing metal-dye complexes have been made by IG by using azo dyes containing sulfonamido groups in place of sulfonic groups. They were claimed to dye wool from a neutral bath uniform shades fast to rubbing, and with a light fastness comparable to the Palatines and wash fastness customary in the Supranol dyestuffs. An example is the dye (XIV), which gives a neutral-dyeing blue complex with chromium. A convenient method for chroming a nonsulfonated dye is to heat it with formamide or ammonium formate, the chromium salt, and a little water at 100–120°.[1, 3]



(XIV)

[1,3] See p. 523.

The Perlon Fast dyes (Table IV) of the IG are special azo dyes for nylon, not containing sulfonic groups, and therefore free from excessive affinity. The dyes are metal-complexes, yielding shades with high light fastness. Some contain sulfonamide groups imparting water-solubility, but others are aqueous dispersions. While the complexes are mostly chromium derivatives, a few (marked Co) are cobalt compounds.[1, 3]

TABLE IV

CONSTITUTION OF PERLON FAST DYES FOR NYLON

Perlon Fast	*Azo dye*
Yellow G	Anthranilic acid → (XIII)
Yellow R (Co)	(III) → Acetoacetanilide
Orange R (mixed azo dye)	Anthranilic acid + (III) → (XIII)
Orange RRS	(III) → (*m*-Sulfamido-XIII)
Red G (mixed azo dye)	(III) + 5-Nitro-2-aminophenol → (XIII)
Red B	5-Nitro-2-aminophenol → (XIII)
Red BS	5-Nitro-2-aminophenol → (*m*-Sulfamido-XIII)
Red 3BS (Co)	2-Aminophenol-4-sulfonamide → β-Naphthol
Violet RTS	(IV) → 2-Naphthol-6-sulfonamide
Violet BT (Co)	5-Nitro-2-aminophenol → β-Naphthol
Dark Blue RS	(IV) → 1-Naphthol-3-sulfonamide
Marine Blue RS	Dark Blue RS + Blue FFB + Green BT
Gray B	5-Nitro-2-aminophenol → β-Naphthol

RECENT TRENDS

The patent literature on soluble chromium complexes of azo dyes up to 1939 has been reviewed by Boyle,[35] and the following examples illustrate more recent trends in this field.

Chromium complexes dyeing yellow on wool are usually prepared from dyes obtained by coupling a diazotized *o*-aminophenol derivative with acetoacetarylides or a 5-pyrazolone.[36] Chromium complexes which give yellow shades of excellent fastness to light can also be obtained by coupling *o*-hydroxy-diazonium salts with β-diketones, e.g., acetylacetone. Azo dyes prepared by coupling (VIII) and similar diazonium components with aroylacetonitriles (ArCOCH_2CN) form stable chromium complexes, which dye wool yellow to violet. The chromium complexes contain one atom of chromium per mole of azo dye, and they have much more color value

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[1,3] See p. 523.

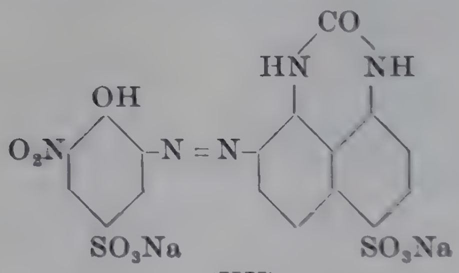
[35] *Am. Dyestuff Reptr.* **28,** 741 (1939); see also Crossley, *ibid.* 487, for a review of some developments in the manufacture of metallized (copper, chromium, nickel, cobalt and iron) dyes and of the spectral changes produced by metallization.

[36] Tables I and II; Mackenzie and American Cyanamid, USP 2,305,095.

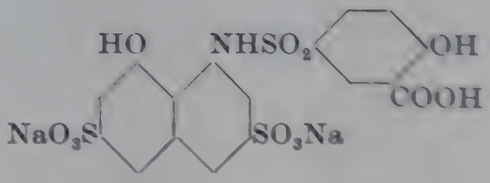
than the unmetallized dyes. The stability of the azo dyes and their chromium complexes to prolonged boiling of the aqueous solution at a pH of 1–4 is noteworthy, since the parent nitriles are not stable under these conditions, and the azo dyes derived from acetoacetanilide, although they are readily convertible into partially chromed dyes, are decomposed when the aqueous solutions are boiled under acid conditions in order to form the completely chromed dyes.[37] The nitriles are conveniently prepared by condensing the esters ArCOOEt with acetonitrile in presence of sodium methoxide[37] or ethoxide.[38]

The primary complex, obtained by treatment of the azo dye (anthranilic acid—→*p*-sulfo-XIII) with a chromium salt in slightly acid medium, levels badly; but the crystalline secondary complex produced from the primary complex under strongly acid conditions dyes clear and level yellow shades fast to light and washing.[39]

Metallized pyrimidine derivatives which dye wool in fast level shades are prepared by coupling a diazotized *o*-aminophenol with 1,8-diaminonaphthalene-4-sulfonic acid and then phosgenating. An example is the chromium complex of (XV). Orange to red shades are produced by the chromium complexes of dyes in which 2,4-dihydroxyquinoline is the second component.[40]



(XV)



(XVI)

The complexes, prepared by heating with chromium lactate the azo dyes obtained by coupling diazotized picramic acid or (I) with the H-acid derivative (XVI), dye silk in fast blue shades. The copper and chromium-copper complexes afford violet shades when printed on cotton and viscose.[41] The chromium complex, which dyes wool in bright blue shades, of the azo dye (VI—→Chicago acid) is obtained by adding an aqueous solution of basic chromium acetate to the dye solution, acidifying with sulfuric acid, boiling for 15 hours, and salting out.[42] When 2,3,6-trichloroaniline-5-sulfonic acid is diazotized, treated with sodium carbonate and coupled with

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[37] Long, *JACS* **69,** 990 (1947).

[38] Dorsch and McElvain, *ibid.* **54,** 2960 (1932).

[39] Kuhlmann, BP 544,673.

[40] Crossley, *Am. Dyestuff Reptr.* **27,** 124 (1938).

[41] Durand and Huguenin, BP 493,883.

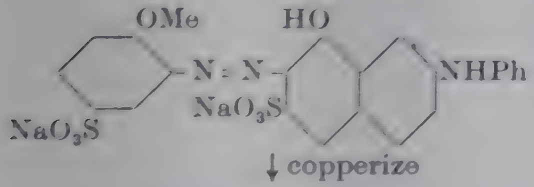
[42] West and Lewis, USP 2,421,737.

5,8-dichloro-1-naphthol, an azo dye with two hydroxyls both *ortho* to the azo group is produced; the soluble chromium complex obtained by boiling the dye with sodium chromium tartrate dyes wool in fast blue shades.[43] The chromium complex of the dye (II ——→2-amino-6-methoxynaphthalene) dyes wool pure yellowish green of good fastness to light and fulling.[44]

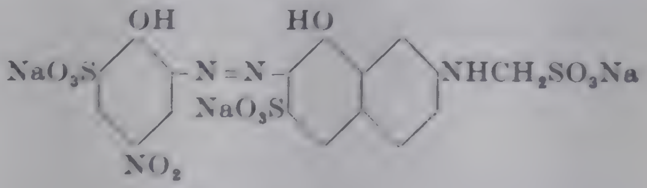
Primary disazo dyes ($A^1 \longrightarrow Z \longleftarrow A^2$) in which Z is resorcinol or 1,5-dihydroxynaphthalene are suitable for the preparation of metal complexes, if A^1 is an *o*-aminophenol. A dye leading to a brown chromium complex is (III——→resorcinol←——Laurent acid), and dyes of this type give in general rich tones of brown on wool with good to excellent fastness to light.[45]

METAL COMPLEXES FOR LEATHER DYEING

Copper complexes suitable for leather dyeing have been described. Thus Igenal Brown IRBF (IG) is the copper complex of the monoazo dye (*o*-anisidine-4-sulfonic acid——→phenyl-γ-acid) prepared by heating the dye in aqueous solution with copper sulfate and ammonia. Shaded with other brown dyes, it is marketed as Igenal Brown IRB (IG), which has good leveling and penetrating power on vegetable-tanned and chrome leather, as well as good fastness.[3] Polyazo dyes of this type are prepared by coupling *m*-diamino-, hydroxyamino- or dihydroxy-benzenes, capable of coupling at least twice, with two diazotized amines, of which the first has a hydroxyl, alkoxyl or carboxyl group *ortho* to the amino group and the second may be a diazoazo compound prepared from an aminodiphenylaminesulfonic acid with any middle component. The disazo dyes may be further coupled to form a trisazo dye, and brown to black shades are produced. In an example resorcinol is coupled with diazotized 2-aminophenol-3-sulfonic acid, converted into a copper complex, which is then coupled with one mole of diazotized 4-amino-4′-nitrodiphenylamine and one mole of diazotized anisidine; the patent[46] states that the trisazo dye can be further coupled with diazotized *p*-nitroaniline, but the coupling position is not clear. Many of the chromium complexes for wool are suitable for leather dyeing, and the IG marketed some of the Palatine Fast colors



Igenal Brown IRBF



(XVII)

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[43] Ciba, BP 541,692.

[44] Ciba, BP 589,146; USP 2,456,230.

[45] Crossley and Shafer, USP 2,034,390; 2,086,854; 2,120,799.

[3] See p. 523.

[46] IG, BP 519,326.

for leather dyeing under the name of Erganil dyes. Erganil Gray GG, introduced in 1943, is prepared by boiling an aqueous solution of the monoazo dye (XVII) with chromium fluoride for 10 hours. The level greenish gray shades on chrome leather and chamois have good fastness to light, acid and alkali.[3] A series of Erganil dyes is listed in Table V.

TABLE V

AZO DYES CORRESPONDING TO THE ERGANIL DYES[5]

Erganil	*Azo dye*
Yellow RCN	*m*-Tolidine ⇉ 2 Moles of (2′-Hydroxy-3′-carboxy-5′-sulfo-XIII)
Orange GGC	Metanilic acid → 8-Hydroxyquinoline
Blue BCC	2 Moles of 6-Chloro-2-aminophenol-4-sulfonic acid → Di-J-acid
Light Brown C	5-Amino-3-sulfosalicylic acid → Resorcinol
Red Brown C	Azol Printing Brown 3RL
Medium Brown C	(XII) → 4-Chloro-*m*-phenylenediamine
Dark Brown C	4,6-Dinitro-2-aminophenol → *m*-Phenylenediamine-4-sulfonic acid
Dark Brown CN	4,6-Dinitro-2-aminophenol → Resorcinol ← *o*-Toluidine-5-sulfonic acid
Gray GG	(XVII)
Gray BC	*o*-Anisidine → 1,7-Dihydroxynaphthalene-3-sulfonic acid[6]
Black C	(IX) → Resorcinol ← (IV)

Like other sulfonic acids, the metal complexes can form arylamine salts by treatment with arylamines or their hydrochlorides under specific conditions; these salts are insoluble in water, but some are soluble in alcohol and other organic solvents, and may be used as spirit-soluble colors. The salts precipitated by the addition of a disubstituted guanidine to the metal complexes of *o*-hydroxyazo dyes have been stated to have uses in the dyeing of paper, wool and leather.[47] The olive-brown iron complex (XII $\xrightarrow{Fe(OH)_3}$ 1,3-dihydroxynaphthalene ← *p*-nitroaniline) is a leather dye.

COPPER COMPLEXES OF DIRECT COTTON DYES

The fastness of direct cotton dyeings to light and washing may be improved in some cases by aftertreatment of the dyed material with copper and chromium salts, but such methods have the obvious disadvantage of introducing an additional process, and a great advance in direct cotton dyes is the production of soluble copper coordination complexes of azo dyes, which are applicable to cellulose fibers by the ordinary direct dyeing process, the shades possessing high fastness to light (6–7). Some of the Sirius and Sirius Supra dyes (IG), the Chlorantine Fast dyes (Cb) and Durazol dyes (ICI) (e.g., Durazol Fast Rubine B, Fast Violet 2B and Blue 2G)[28] belong to this type. As substantive dyes they possess the usual structural characteristics and are in addition derived from a diazotized *o*-aminophenol or other component enabling the preparation in substance of a stable metallic coordination complex.

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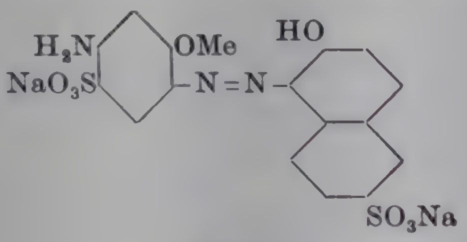
[3] See p. 523.

[5] See p. 523.

[6] See p. 523.

[47] Daudt, Hannum and du Pont, USP 2,165,034.

The constitution of several of the copper complexes in the Sirius Supra range of the IG has become available.[2] Sirius Supra Rubine BBL (copper complex of the disazo dye: Two moles of *o*-anisidine-4-sulfonic acid $\rightrightarrows$ carbonyl-J-acid) has a light fastness of 7. Sirius Supra Red-Violet RL is the copper complex of the disazo dye obtained by phosgenation of the monoazo dye (XVIII). The copper complex is marketed as the ammonium salt of the sulfonic acid. It has a light fastness (7–8) which is only equalled by some of the anthraquinonoid vat colors. Sirius Supra Violet BL is the copper complex of the disazo dye (two moles XIX $\rightrightarrows$ di-J-acid). Sirius Supra Blue FBGL is the copper complex, prepared by the prolonged agitation of a mixture of the disazo dye (ε-acid←—dianisidine—→phenyl-J-acid), copper sulfate, sodium acetate and water. The homogeneous mixture is dried *in vacuo* at 120–125°. Sirius Supra Blue GL, which has light fastness 7, but fastness to washing only 1–2, is the copper complex of Dianil Blue G prepared by mixing the dye into a homogeneous mass with aqueous copper sulfate and ammonia in a Baker-Perkin type of kneader-mixer, and drying down the paste *in vacuo* at 120–125°. Treatment of the disazo dye (XX) with ammoniacal copper sulfate at 90° gives Sirius Supra Blue 3RL which has a light fastness of 6, combined with good fastness to washing (3), considering that it is a direct cotton dye. Sirius Supra Green BTL is a



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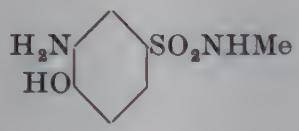

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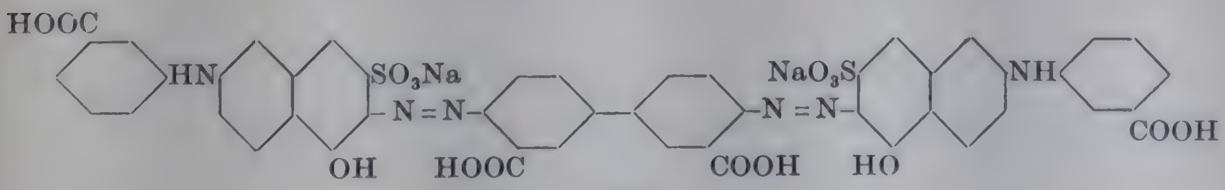

(XX)

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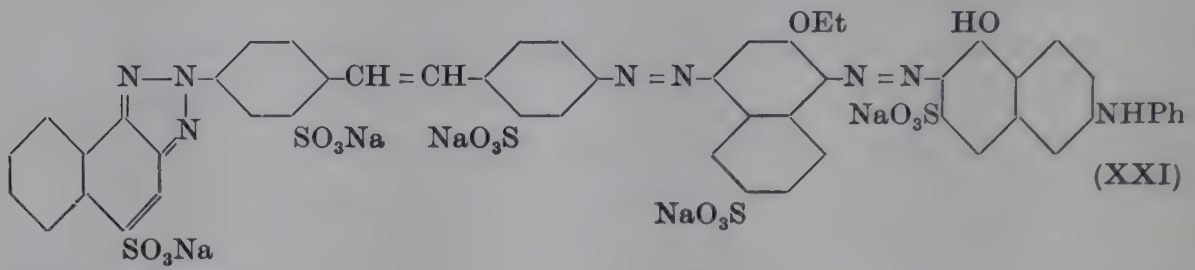
[28] See p. 534.

[2] See p. 523.

valuable addition to the range of direct cotton dyes;[3] it dyes cotton, viscose and union fabrics of cotton, viscose and wool level shades with excellent fastness to light (6–7) and good fastness to washing (3–4) at 40°. It is prepared by heating (XXI) with an aqueous solution of copper sulfate, sodium acetate and acetic acid in an autoclave at 120–125° for 2–3 hours. The triazole (XXII), from which (XXI) is obtained by the scheme (XXII



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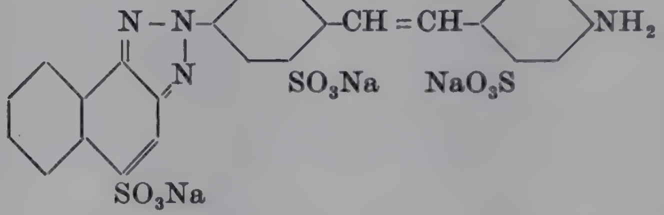
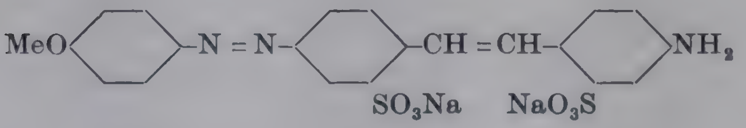


(XXII)

⟶2-ethoxy-1-naphthylamine-6-sulfonic acid ⟶phenyl-J-acid), is prepared by ammoniacal copper sulfate oxidation of the *o*-aminoazo compound (4-nitro-4′-aminostilbene-2,2′-disulfonic acid⟶naphthionic acid), followed by reduction of the nitro compound to the amine (XXII) by iron and acetic acid. Sirius Green GT is the copper complex of the dye (XXIII⟶2-ethoxy-1-naphthylamine-6-sulfonic acid⟶*N*-3′-carboxyphenyl-J-acid).[6] Sirius Supra Brown BRS, which has a light fastness of 6 and a fastness



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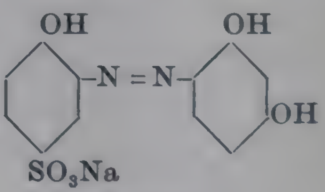

(XXIV)

of 2–3 to other agencies, is a copper complex of a trisazo dye in which the coppering is carried out at an intermediate stage. The monoazo dye (XXIV) is converted into a copper complex by heating at 85° with an alkaline solution of copper sulfate and precipitating by acid. The trisazo dye is then prepared by the scheme (copper complex of XXIV⟵benzidine ⟶salicylic acid). Sirius Supra Brown BRLN is a similar dye in which salicylic acid is replaced by a mixture of this acid (82%) and *o*-cresotinic acid (18%).[2] Sirius Supra Brown 5G is (amido-G-acid⟶*m*-toluidine;

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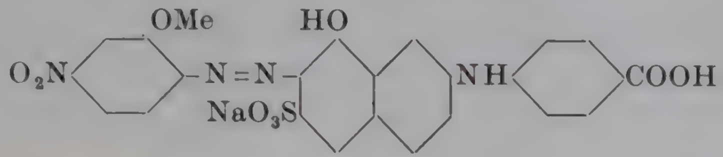
[3] See p. 523.

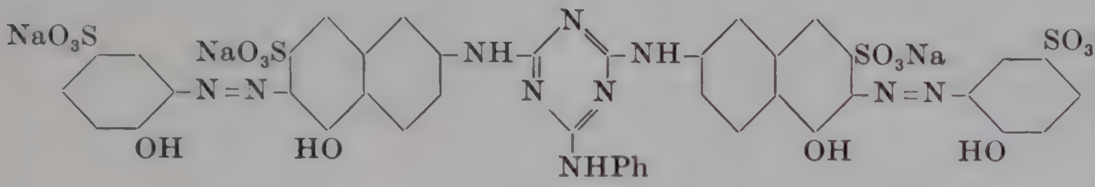
[6] See p. 523.

[2] See p. 523.

condense with *p*-nitrobenzoyl chloride; reduce; and⟶copper complex of XXIV). Sirius Supra Olive GL is the copper complex of the trisazo dye (XXIII⟶2-ethoxy-1-naphthylamine-6-sulfonic acid⟶acetyl-S-acid). Sirius Supra Gray VGL is the copper complex of the trisazo dye obtained by glucose-alkali reduction of (XXV).[2]


(XXV)

Chlorantine Fast Rubine RLL (Cb) is a copper complex of the cyanurated azo dye (XXVI).[48]

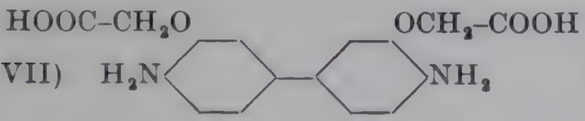

(XXVI)

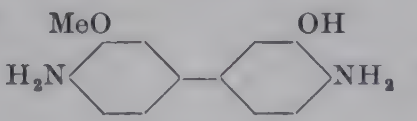
Recent patent literature gives ample evidence of the importance of this new class of metalliferous direct cotton dye.

Yellow copper complexes for cotton and viscose are obtained by linking one mole of dehydrothiotoluidine sulfonic acid and one of 3′- (or 4′) -amino-1-phenyl-5-pyrazolone-3-carboxylic acid by means of phosgene or cyanuric chloride, coupling with a diazonium salt having an *o*-carboxyl, and converting into the metal complex.[49]

3,3′-Dihydroxybenzidine and its biscarboxymethyl derivative (XXVII) are useful for the preparation of copper complexes. Thus yellow to orange

(XXVII)




(XXVIII)

dyes for cotton and viscose from tetrazotized (XXVII) can be converted into metal complexes or aftertreated with metallic salts on the fiber,[50] and 3-hydroxy-3′-methoxybenzidine (XXVIII) can be used for similar purposes.[42] *o*-Dianisidine is partially demethylated to (XXVIII) by prolonged boiling with 65% sulfuric acid at 140°. Disazo dyes from tetrazotized dianisidine (or *o*-diethoxybenzidine) afford copper complexes if the second components are naphthol- and aminonaphtholsulfonic acids in which *o*-coupling takes place, such as the dye (ε-acid⟵dianisidine⟶ Chicago acid). On boiling this dye with aqueous copper sulfate and ammonia for a few hours, the blue complex can be salted out.[51] When one of the end components is the monoazo dye (anilinesulfonic acid $\xrightarrow{\text{acid}}$ S-acid), triazole cyclization and copper-complex formation can be effected in one operation.[52] Complexes prepared from *o*-hydroxy-*o*′-methoxyazo compounds yield much brighter shades on cotton, if metallic copper is added to the copperizing solution of ammonia and a copper salt.[53]

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[2] See p. 523.

[48] Ref. 25, Chapter XVI.

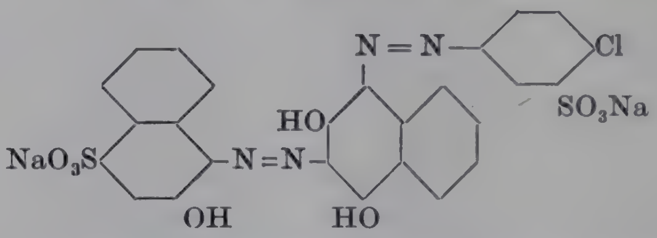
[49] Ciba, BP 515,099.

[50] IG, BP 518,896; see also Ciba, USP 2,427,537; 2,426,977; 2,427,534; 2,424,066; 2,428,130; 2,476,261.

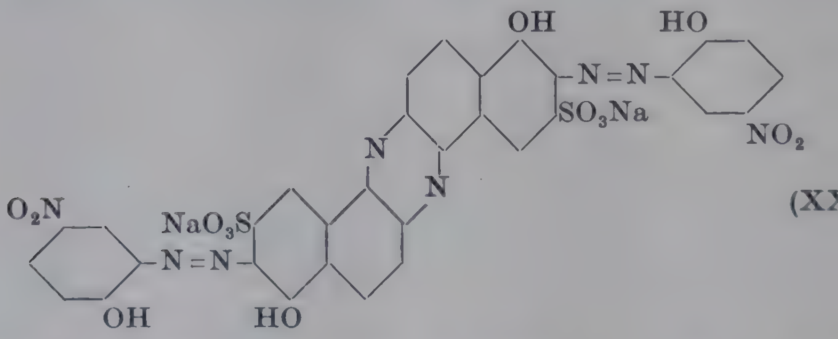
[42] See p. 542.

Naphthoresorcinol (1,3-dihydroxynaphthalene) is suitable for the preparation of disazo dyes (e.g., XXIX), which are metallizable and are substantive to cotton.[54]

The bisamides of 2-naphthol-6-carboxylic acid condensed with benzidine, or the monoamide with J-acid, are coupled with *o*-aminophenolsulfonic acids and converted into copper complexes which are red dyes for cotton.[55] Disazo dyes convertible into copper complexes are obtained by coupling the urea of J-acid with one mole of a diazotized anthranilic acid and one mole of diazotized 6-chloro-2-aminophenol-4-sulfonic acid; the bluish red dyes are claimed to have excellent substantivity and fastness.[56] The tetrakisazo dye (two moles 4-amino-4′-hydroxyazobenzene-3,3′-dicarboxylic acid $\Longrightarrow$ di-J-acid) forms metal complexes which are suitable for dyeing or printing cellulose fibers.[56a] Another azo dye suitable for metallization, in which the second component is a J-acid derivative, is (XXX). The



(XXIX)



(XXX)

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[51] du Pont, BP 575,437; 575,475; USP 2,437,699; see also Ciba, BP 609,299; 609,302; Schedler, Whalley, and Clayton Aniline Co., BP 608,115; 613,939; 615,210; 628,028; Sandoz, BP 597,130; 633,206; SP 243,334.

[52] American Cyanamid, USP 2,390,480.

[53] Allied Chemical and Dyestuff, USP 2,400,092.

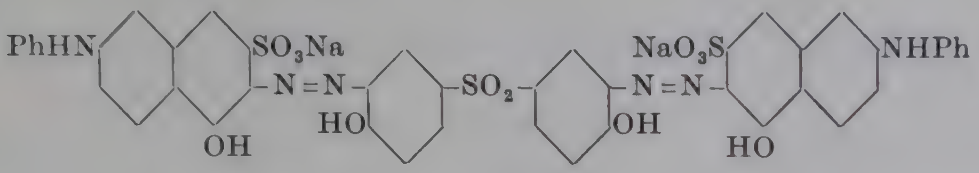
[54] Straub, Brassel, Mayer, and Ciba, USP 2,408,961; Kuhlmann, BP 540,125.

[55] IG, BP 519,326.

[56] Geigy, BP 562,641.

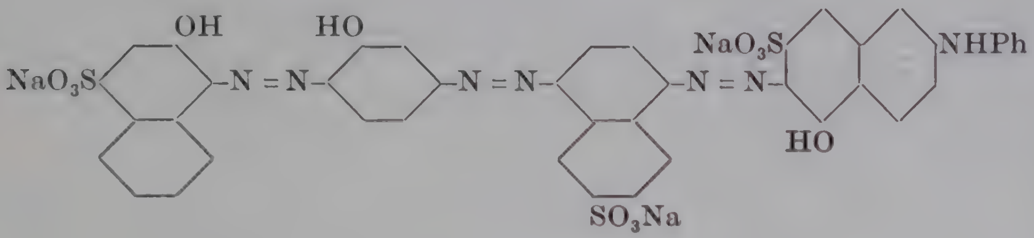
[56a] Ciba, BP 616,977.

copper complex of the disazo dye (XXXI) dyes red-violet on cotton; the primary component is an interesting variation of the usual *o*-aminophenol derivatives, being a symmetrically constituted diphenylsulfone.



(XXXI)

The trisazo dye (XXXII) gives a copper complex which dyes cotton and viscose in blue shades fast to light and washing. The copper complex



(XXXII)

may be prepared by the scheme (1-naphthylamine-6-sulfonic acid←—2,5-diaminophenol—→2-naphthol-4-sulfonic acid; copperize and—→phenyl-J-acid in pyridine solution). Using the monoazo dye (5-aminosalicylic acid $\xrightarrow{\text{acid}}$ J-acid) as the end component, the dye is greenish gray-blue.[57]

Gray and green trisazo dyes of the pattern (salicylic acid←—D—→M —→an N-substituted J- or γ-acid) have been converted into copper complexes. Another scheme, leading to blues, is (*o*-aminophenol—→2,5-dimethoxy(or ethoxy)-aniline—→arylamine—→J-acid or 1-arylazo-J-acid); the dyes may be coppered in substance or on the fiber, or the copper complex of the monoazo dye may be diazotized and used for the second coupling.[58]

Metal complexes for cotton dyeing can be prepared from stilbene-azo dyes, and while stilbene-azo dyes themselves are normally yellow, orange and brown dyes notable for their fastness to light, copper complexes of such dyes containing conventional metallizable groups yield fast to light shades of brown, gray, olive, and green. One type of structure for green coppered disazo dyestuffs is based on the use of a 2-alkoxy-Cleve acid as middle component and an *o*-coupling naphthol derivative as end component, the first diazonium components being aminostilbene-naphthotriazoles.[59]

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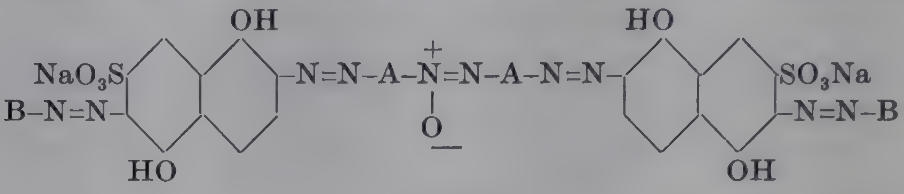
[57] Sandoz, BP 571,334; USP 2,427,539; 2,472,965. See also SP 227,497-506.

[58] Geigy, BP 551,278; SP 215,059-67. See also SP 226,608-18.

[59] IG, BP 503,576.

The few commercial dyes derived from 1,5-dihydroxynaphthalene are monoazo dyes, but the copper complexes of the tetrakisazo dyes (XXXIII) have been described. The azoxy group is produced by reduction of a nitro group in A. Both A and B are aromatic radicals containing a metallizable group in the *o*-position.



(XXXIII)

IG have synthesized cotton dyes which contain both coordinated copper and trivalent chromium, thereby resulting simultaneously in enhanced light and washing fastness.[1]

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[1] See p. 523.

CHAPTER XIV

CONSTITUTION OF METAL-DYE COMPLEXES

From a study of such compounds as the ferrocyanides, ferricyanides and ammines, Werner (1891) suggested that when the principal valencies have been satisfied an atom can still combine or coordinate with other atoms, groups or molecules, and form complexes. The maximum number of atoms, groups or molecules which can be thus attached to a central atom (coordination number) is usually four or six. When the coordination number is 6, the units arrange themselves in octahedral symmetry around the central atom; when it is 4, plane and tetrahedral configurations are possible. The complex of the central atom and the coordinated units as a whole may be neutral or anionic or cationic; the number and the sign of the charge on the complex depend on the character of the units linked to the central atom in the coordination sphere. The electronic interpretation of the constitution of the Werner compounds is based on the extranuclear electronic structure of the central atom and its tendency to assume the electronic configuration of the nearest inert gas.[1, 2] The transition metals enter into coordination complexes most readily, since their ions have low-lying vacant orbitals and are facile electron-acceptors. The atoms, groups or molecules united to the central atom in Werner's " first sphere of coordination " are in covalent combination; the linkage may be normal covalency or coordinate covalency. The electronic contributions made by the units attached to the central atom then determine the magnitude and sign of the charge on the complex, and therefore its ability to form salts with anions or cations. It is not necessary that the central atom should be linked to the number of groups that are theoretically possible, and it can be coordinatively unsaturated.

Chromium compounds. Trivalent chromium has the coordination number 6; in addition to the three electrovalencies, six atoms or groups can attach themselves to the metal by covalent combination. In the seven types of chromic compounds indicated below, G is a neutral group or molecule, such as water, ammonia or the azo group, which donates a pair of electrons to the central atom; X is a monovalent anion; and M a monovalent metal or other cation.

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[1] For a recent account of the structure of coordination compounds, see Fernelius in Frontiers in Chemistry, Vol. V, Interscience Publishers, New York, 1948.

[2] See also Pauling, The Nature of the Chemical Bond, 2nd ed., Cornell Univ., 1940; *JCS* 1461 (**1948**).

Since the atomic number of chromium is 24 and the chromic ion has the extranuclear electronic structure 2.8.11, the formation of coordination complexes by association with 12 electrons does not result in the attainment by the central metallic atom of the electronic structure of krypton; there is a deficiency of three electrons, unlike the corresponding cobaltic complexes in which cobalt (atomic number 27) attains the krypton configuration.

Type	*Example*
(1) $[\mathrm{Cr\ 6G}]^{+++}\ \mathrm{X}_3^{---}$	$[\mathrm{Cr(H_2O)_6}]\mathrm{Cl_3}$
(2) $[\mathrm{Cr\ 5G\ X}]^{++}\ \mathrm{X}_2^{--}$	$[\mathrm{Cr(OH)\ (H_2O)_5}]\mathrm{Cl_2}$
(3) $[\mathrm{Cr\ 4G\ 2X}]^{+}\ \mathrm{X}^{-}$	$[\mathrm{Cr(H_2O)_4Cl_2}]\mathrm{Cl}$
(4) $[\mathrm{Cr\ 3G\ 3X}]$	$[\mathrm{Cr(OH)_3(H_2O)_3}]$
(5) $[\mathrm{Cr\ 2G\ 4X}]^{-}\ \mathrm{M}^{+}$	$\mathrm{Na}[\mathrm{Cr(NH_3)_2(OOC{-}COO)_2}]$
(6) $[\mathrm{Cr\ G\ 5X}]^{--}\ \mathrm{M}_2^{++}$	$\mathrm{K_2}[\mathrm{Cr(H_2O)F_5}]$
(7) $[\mathrm{Cr\ 6X}]^{---}\ \mathrm{M}_3^{+++}$	$\mathrm{K_3}[\mathrm{CrF_6}]$

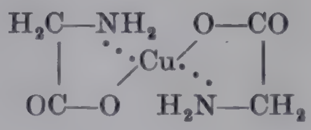
Copper complexes. The normal coordination number of copper (atomic number 29) is four. In the cupric copper complexes, the central metallic atom is one electron short of the electronic structure of krypton.

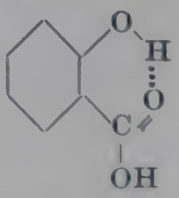
The types of coordination compounds formed by bivalent copper are as follows: (1) $[\mathrm{Cu(G_4)}]\mathrm{Cl_2}$; (2) $[\mathrm{Cu(G_3)X}]\mathrm{Cl}$; (3) $[\mathrm{Cu(G_2)(X_2)}]$; (4) $\mathrm{M}[\mathrm{Cu(G)(X_3)}]$; (5) $\mathrm{M_2}[\mathrm{Cu(X_4)}]$.

CHELATE COMPOUNDS

It is possible for coordination to take place between two atoms that already form part of the same molecule. The product then contains a heterocyclic ring, and examples are copper compounds of glycine (I) and acetylacetone. Such ring formation is described as chelation (from the Greek word for claw).[3] In addition to this twofold attachment, threefold and fourfold attachments of a molecule to a metal atom are known; e.g., α, β, γ-triaminopropane can replace three molecules of ammonia in a cobaltammine. Intramolecular hydrogen bonding, e.g., in salicylic acid (II), is a type of chelation. Such chelate rings are usually six-membered, and there is the possibility of two electronic configurations giving rise to resonance.[4] The mordant dyes, containing salicylic acid residues, *o*-hydroxyazo groups and *o*-hydroxycarbonyl groups, are characterized by the presence

(I)





(II)

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[3] Morgan and Drew, *ibid.* **117,** 1457 (1920); Diehl, *Chem. Revs.* **21,** 39 (1937).

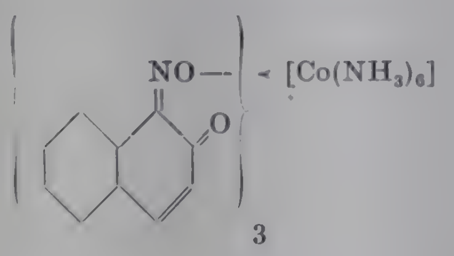
[4] Rodebush in Advances in Nuclear Chemistry and Theoretical Organic Chemistry, Interscience Publishers, New York, 1945, p. 151.

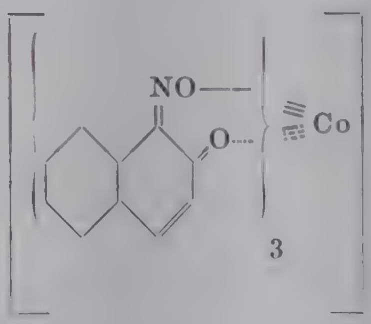
of hydrogen-bonded chelate rings, and in the process of mordant dyeing the hydrogen atoms concerned are replaced by metal atoms capable of forming coordination complexes.

Coordination compounds containing chelate groups often exhibit, in addition to loss of ionizing power and the absence of the usual analytical reactions of the metallic atom, abnormal color, sparing solubility in water, solubility in organic solvents and volatility without decomposition. For instance, the thorium salt of acetylacetone can be distilled without decomposition, and many copper salts of β-diketones, *o*-hydroxyazo compounds, etc., can be crystallized from organic solvents. Chelate compounds (e.g., chlorophyll and hemoglobin) are important in biological oxidation-reduction systems, and the oxygen-carrying properties of certain synthetic chelate compounds (e.g., the cobalt compound from salicylaldehyde-ethylenediamine) have been studied.[5]

Dyes which form stable coordination complexes with metals belong to three main types; (1) azo dyes; (2) quinoneoximes; and (3) hydroxyanthraquinones. All have the common feature of one or more chelate groups, and in general the chelate ring formation is between an azo or carbonyl group on the one hand, and on the other a metal atom (e.g., chromium or copper) covalently attached to the oxygen atom of a phenolic or enolic hydroxyl group. Our knowledge of the constitution of metal-dye complexes is mainly due to Pfeiffer, Morgan and Main Smith,[6, 6a] and Drew. When hexamminocobaltic chloride and the sodium salt of 1-nitroso-2-naphthol react in aqueous solution at room temperature, a sparingly soluble dark green hexamminocobaltic 1,2-naphthoquinone-1-oximate (III) is

(III)





(IV)

precipitated; on warming to 40°, all the ammonia is lost, and (III) passes quantitatively into the stable cobaltic lake (IV) from which the cobalt is no longer removable by ammonia or other alkali. The lake is no longer capable of combination with ammonia and the coordination number of cobalt has therefore been completed by three molecular proportions of the nitrosonaphthol radical functioning in the tautomeric form of 1,2-naphthoquinone monoxime. Hence each molecule of the dye behaves as a chelate group, both the ketonic and isonitroso limbs of the chela being in direct association with the central cobalt atom.[6, 7]

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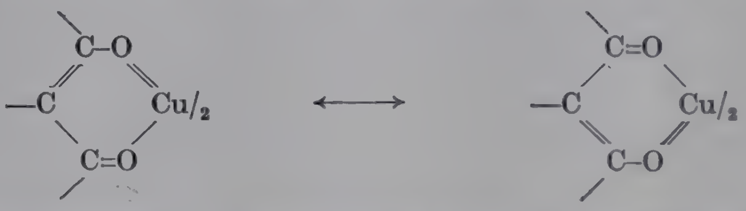
[5] Calvin *et al.*, *JACS* **68**, 2254 (1946); *et sequa.*

[6] *Ber.* **44**, 2653 (1911); *Ann.* **398**, 139 (1913); *et sequa.* Morgan and Main Smith, *JCS* **119**, 704 (1921); **125**, 1731 (1924).

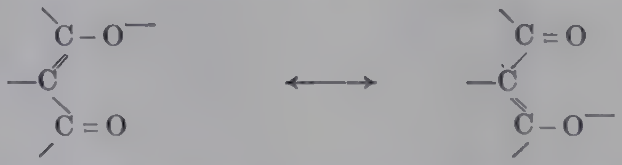
[6a] See also Pfitzner, *Angew. Chem.* **62**, 242 (1950).

Calvin and Wilson[8] have made a quantitative study of the influence of structural factors on the stability of chelate compounds. For a series of twenty-one chelate compounds of copper, derived from acetylacetone, salicylaldehyde and 2-naphthol-1- and 3-aldehyde, in which bivalent copper is bound to four oxygen atoms, they have determined the stability against dissociation into the component ions. Their character as bases and a resonance effect involving the copper are important in determining the stability of the compounds. In this type of chelate compounds, an important contributor would be a completely conjugated 6-membered ring (V) analogous to benzene, pyridine or the pyrylium salts. The availability and geometry of orbitals of the metal have to be considered in



(V)

relation to the differences in the chelating ability of different metals. Calvin and Wilson have calculated the bond order of the C=C bond in the 3-carbon system forming the conjugate chain between the two oxygen atoms in the four types of compounds studied by them, and have shown that with decreasing double-bondedness of the bond there is a decrease in the stability of the copper compounds at a constant acidity of chelating agent.



(VI)

They conclude that the enolate resonance (VI) plays a different and far greater part in the bonding of copper than it does in the bonding of hydrogen.

COORDINATION OF THE AZO GROUP

The azo group has not been observed to coordinate with a metallic atom to form a stable complex unless the metal can be held by chelation within the dye molecule. Mordant azo dyes must therefore possess a

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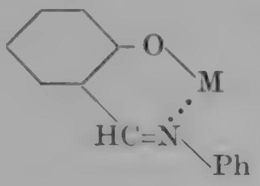
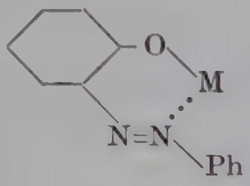
[6] See p. 553.
[7] Morgan and Main Smith, *J. Soc. Dyers Colourists* **41**, 233 (1925).
[8] *JACS* **67**, 2003 (1945).

hydroxyl, amino or other group in the *o*-position to the azo group to enable the metal atom to be implicated in a chelate ring. Further, only one nitrogen atom of the azo group enters into coordination; copper complexes have been assigned structures in which both the nitrogen atoms of an azo group coordinate with the metallic atoms,[9] but such complexes are to be regarded as resonance hybrids of azo and quinonehydrazone structures. The existence of the metal complexes of *o*-hydroxyazo compounds indicates the *trans* arrangement of the groups attached to the azo group.[10] By analogy with the metal derivatives (I) of salicylideneaniline in which the coordination of the metal M[11] and the nitrogen atom must result in a 6-membered chelate ring, the structure (II) for the metal complexes of *o*-hydroxyazo dyes is generally assumed; but (I) and (II) are not strictly analogous, since the azomethine group has only one donor atom. Studies of the stereochemical properties of chelated compounds[12] have shown that 6-membered chelate rings possess somewhat greater stability than 5-membered rings, and considerably more stability than 7-membered rings. Evidence in favor of (II) is provided by the stability of the metallic compounds, their solubility in organic solvents, and their comparatively low melting points, pointing to their character as resonance hybrids of the azo (II) and the quinonehydrazone (III) structures. The resonance necessitates a coplanar configuration for the chelate ring involving the metal atom. With the introduction of a second hydroxyl group *ortho* to the azo group and of one or more sulfonic groups, the configurations of the metal-azo dye complexes become considerably more complicated, and the azo dyes exhibit a remarkable adaptability in the positional adjustments of the azo group and the aromatic nucleus attached to each nitrogen, as a result of which metallic coordination complexes are formed.



(I)



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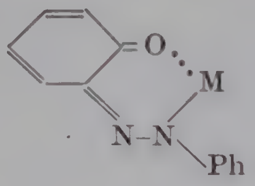

(III)

In transcribing the structures assigned to the metal-dye complexes by Drew and others, a dotted line is used to represent the coordinate bond. This is merely to enable ready reckoning of the charge on the complex, and no difference is implied between the covalent bonds when they have been formed, whether they are represented by a full line or a dotted line.

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[9] Beech and Drew, *JCS* 608 (1940).

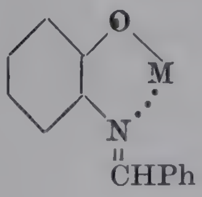
[10] Elkins and Hunter, *ibid.* 1598 (1935).

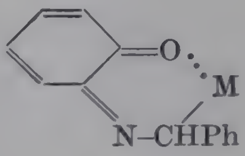
[11] M represents the proportion of the metallic atom implicated in the chelate ring.

[12] E.g., Lassettre, *Chem. Revs.* **20,** 267 (1937); Wulf and Liddell, *JACS* **57,** 1469 (1935).

Discussing the constitution of the coordinated copper salts of *o*-hydroxyazo compounds, Drew and Landquist[13] consider that the 5-ring structure is not excluded in principle, and that it is indeed probable in certain cases; quoting Barrow, they cite the copper derivative of benzylidene-*o*-aminophenol as presumably having the structure (IV), although a 6-ring structure (V) is not excluded.

(IV)





(V)

When the number of electrons associated with the metallic atom in its combination with the azo compound is smaller than the number required for the stable complex (33 for chromium, 35 for copper, 36 for cobalt), the coordinatively unsaturated compound makes up for the deficiency by the attachment of water molecules, ammonia, etc. In the preparation of metal-dye complexes in substance, water is available for this purpose; and in mordant dyeing, electron-donor groups in the protein or cellulose molecule can attach themselves to the metallic atom to form a stable metal-dye-fiber complex.

Ernsberger and Brode[14] have examined the absorption spectra of a series of phenylazo-*p*-cresol, β-naphthol and β-naphthylamine derivatives with methyl, nitro and chloro substituents in the phenyl ring, together with the spectra of their copper, nickel and cobalt compounds. The metal compounds exhibit a new band in the visible region ascribed to the metal, but the metal appears to have little effect on the chromophore of the dye. On the other hand, the new bands in the spectra of the dye-metal compounds occur at the same position for a given metal, regardless of the dye with which it is combined, so that the dye mass has little effect, and the new band is not associated with vibration of the entire molecule. The characteristic absorption maxima of the new bands do not correspond to those of aqueous solutions of the simple metal salts. Data on the molecular weight of some of the metal-dye compounds determined cryoscopically in benzene show that the nickel compounds are monomolecular and undissociated; the cobalt compounds are bimolecular, being probably cobaltic compounds. The copper compounds are probably monomolecular and undissociated.

True mordant azo dyes have sometimes been defined as those which form lakes with metallic mordants without undergoing oxidation; but for the purpose of considering the constitution of their metallic complexes mordant azo dyes may be classified into three groups: (*a*) *o*-hydroxyazo compounds; (*b*) azo dyes in which lake formation involves oxidation to quinonoid forms; and (*c*) azosalicylic acids.

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[13] *JCS* 292 (1938).

[14] *J. Org. Chem.* **6**, 338 (1941).

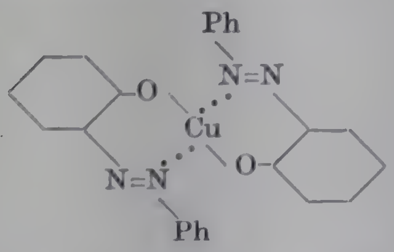
o-HYDROXY- AND *o,o′*-DIHYDROXYAZO DYES

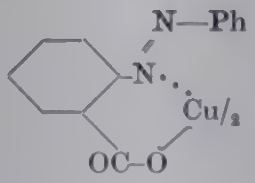
Some of the metal derivatives are crystallizable and easy to obtain in analytically pure form. In such cases the constitution of the complex may be determined without ambiguity. The complexes of some dyes containing sulfonic groups can only be obtained in amorphous form. Purification has to be effected indirectly by removing what appears to be extraneous matter more soluble in solvents than the metal derivative, and its purity has then to be judged by quantitative analysis of the coordinating metal, water of crystallization and coordination, sulfur, nitrogen and other elements after successive stages of purification. Drew's papers provide a valuable guide to the methods by which metal-azo dye complexes may be prepared and purified.

Copper complexes. Haendler and Smith[15] have isolated in the crystalline state a large number of copper complexes of phenylazo-β-naphthols, with methyl, chloro, methoxyl and ethoxyl groups in the phenyl ring in *o*-, *m*- and *p*-positions. The complexes contain a stable 6-membered ring (cf. I). The complexes are brown in color when finely divided, with a greenish or purplish cast when crystalline. The solubility varies over a wider range than the other properties, the *o*-substituted phenylazo compounds being the most soluble; they are so soluble in dioxane, benzene, etc., as to make crystallization extremely difficult. All the complexes are soluble in pyridine, and they are decomposed by concentrated sulfuric acid.

Drew and Landquist[13] have described copper derivatives of *o*-hydroxy, *o*-carboxy-, *o,o′*-dihydroxy-, *o*-hydroxy-*o′*-carboxy-, and *o,o′*-dicarboxyazo compounds of the benzene and naphthalene series, as well as derivatives of *o*-hydroxyazo sulfonic acids. *o*-Hydroxyazo compounds form coordinated

(I)





(II)

cupric compounds of the type (I), as observed also by other workers. An *o*-carboxyl group in azobenzene resembles an *o*-hydroxyl in its ability to form metal chelates. The metal complexes may have the coplanar 6-ring structure (II) or the nonplanar 7-ring structure (III); the attachment of the metal to the azo compound is less stable than in the *o*-hydroxyazo compounds. The copper derivatives of *o*-hydroxy-*o*′-carboxyazo compounds exhibit coordinative unsaturation, being soluble in aniline or pyridine, and forming crystalline derivatives (IV) with one mole of the base. In the case of *o,o*′-dihydroxyazo compounds, Drew has observed that the metallic atom is covalently linked to both the hydroxyl groups. The copper derivative of *o,o*′-dihydroxyazobenzene is coordinatively unsaturated and forms a crystalline monopyridine compound (V), in which the combined base is firmly held.

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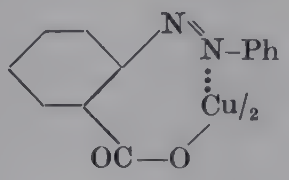
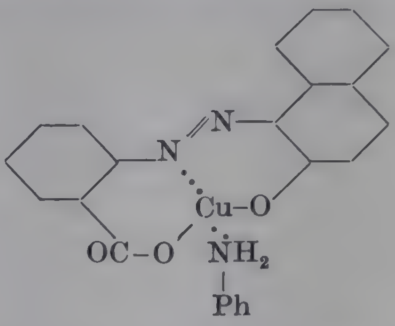
[15] *JACS* **62**, 1669 (1940); see also Haendler and Geyer, *ibid.* **60**, 2813 (1938).

[13] See p. 556.

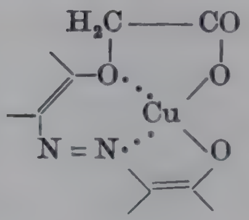
(III)



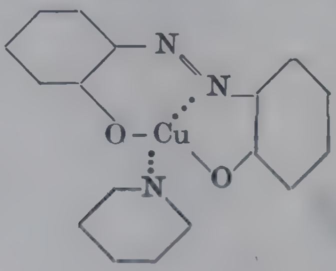


(IV)

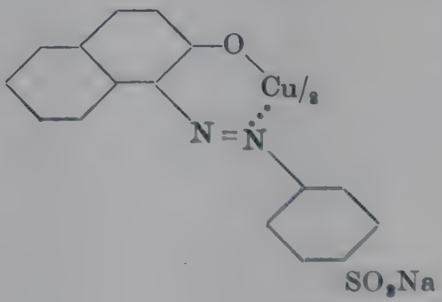
Azo dyes from the *bis*-carboxymethyl derivative of 3,3′-dihydroxybenzidine form copper complexes of the following type.[6a]



The behaviour of *o*-hydroxyazobenzenesulfonic acids towards metallic salts is more complicated than that of the insoluble *o*-hydroxyazo compounds free from sulfonic groups,[9] and is of greater interest since nearly all the technically important mordant azo dyes are sulfonic acids. With copper salts, the sulfonic acids first form the cupric sulfonates. Thus *p*-sulfo-



(V)

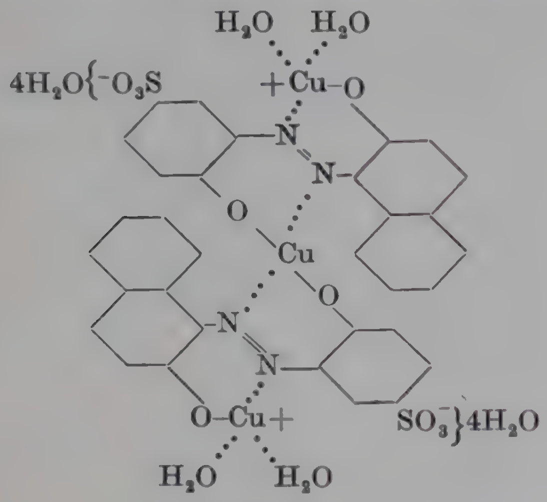


(VI)

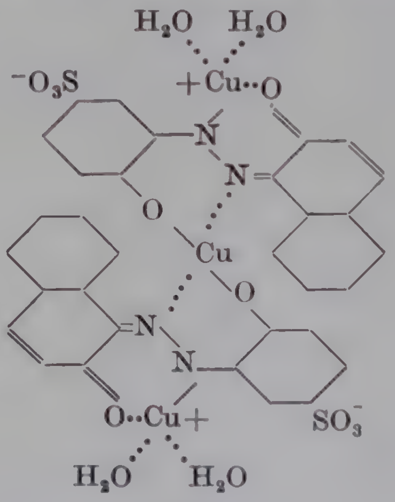
[6a] See p. 553.

[9] See p. 555.

benzeneazo-β-naphthol forms an orange-red salt, strongly hydrated and somewhat readily soluble in water; on treatment with alkali or alkali acetate, the salt is converted into a brownish-red coordination complex (VI), which is soluble in water with a deep brown color. Copper does not enter the inner complex unless the sulfonic group is neutralized by copper or other basic atoms or groups. However, the presence of a single sulfonic group is not sufficient to prevent the formation of an internal complex when there are two hydroxyl groups, both *ortho* to the azo group.[9] When the azo dye (2-aminophenol-4-sulfonic acid⟶β-naphthol) (Copper Red N, MLB) is treated with cupric chloride, a reddish brown cupri-complex dodecahydrate is produced, which on the basis of its content of carbon, hydrogen, copper and water Beech and Drew have formulated as (VII), in which the coordination of both the azo-nitrogen atoms to metal atoms is postulated.

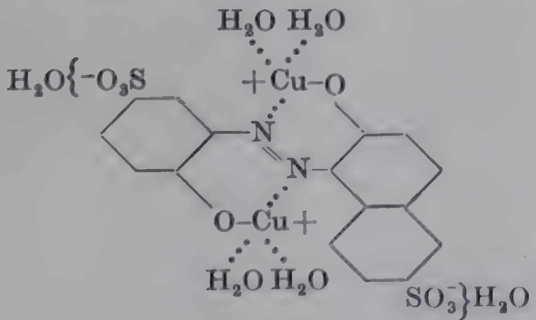

H$_2$O H$_2$O
4H$_2$O{$^-$O$_3$S
+Cu–O
N
N
O
Cu
O
N
N
O–Cu+
SO$_3^-$}4H$_2$O
H$_2$O H$_2$O

(VII)

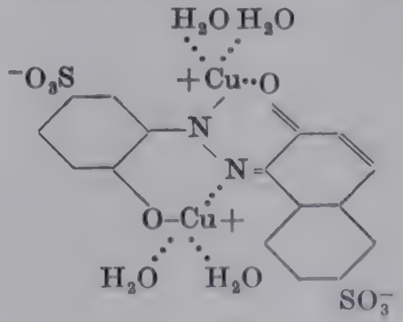

H$_2$O H$_2$O
$^-$O$_3$S
+Cu··O
N
N=
O
Cu
O
=N
N
O··Cu+
SO$_3^-$
H$_2$O H$_2$O

(VIII)

A copper compound (IX) in which two copper atoms are coordinated with one azo group has also been described; it is prepared from the azo dye (2-aminophenol-4-sulfonic acid⟶β-naphthol-6-sulfonic acid). The profound influence of the sulfonic group on the stereochemistry of the coordination complexes will be observable by a comparison of the structures (V) and (VII; IX). In (V) both the hydroxyl groups are on the same side


H$_2$O H$_2$O
H$_2$O{$^-$O$_3$S
+Cu–O
N
N
O–Cu+
H$_2$O H$_2$O
SO$_3^-$}H$_2$O

(IX)


H$_2$O H$_2$O
$^-$O$_3$S
+Cu··O
N
N=
O–Cu+
H$_2$O H$_2$O
SO$_3^-$

(X)

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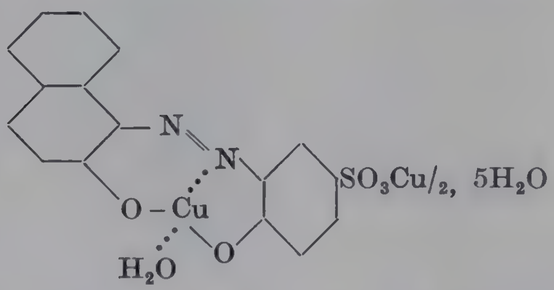
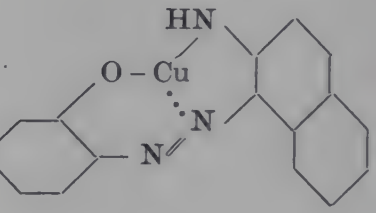
[9] See p. 555.

of the azo link, while in (VII and IX) they are on opposite sides, one of the aromatic nuclei in each azo dye unit undergoing rotation to enable the necessary orientation of the hydroxyl groups to take place. It is now suggested that the complexes formulated by Beech and Drew (VII and IX) are more satisfactorily represented as (VIII) and (X), or as resonance hybrids.[16] When the unshared electron pair of one nitrogen atom of an azo group has been utilized in covalent linkage to a metal atom, the electromeric effect will render the unshared electron pair of the second nitrogen atom less available for attachment of this nitrogen atom to a metal atom (cf. the adjacent charge rule).[2] However, resonance of the structure (VII) with (VIII), and of (IX) with (X), will give the complexes considerable stability.[17] *o,o′*-Dihydroxyazo compounds form coordination complexes much more readily than *o*-hydroxyazo compounds, and in the former case the metal chelates are also markedly more stable; for the metal complexes of *o,o′*-dihydroxyazo dyes, structures in which the metal is held between the azo groups and both the hydroxyl groups are therefore normally to be favored, but the structure (XI) as an alternative for (VII) is untenable since the complex does not contain ionizable copper.

(XI)





(XII)

o-Aminoazo compounds yield coordination complexes if a hydroxyl or carboxyl group is present in the *o′*-position. An example is the coordinatively unsaturated copper complex (XII), which combines with pyridine to form a well-crystallized monopyridine derivative.[9]

Chromium complexes. A single *o*-hydroxyl group is insufficient to hold a chromium atom in stable combination with azo-nitrogen; this is also true of iron, manganese and zinc, and in contrast with the behavior of copper, nickel and cobalt from which coordination complexes of *o*-hydroxyazo compounds have been prepared. As against the greater stability of copper-azo coordination in the monohydroxyazo compounds, the chromium complexes of *o,o′*-dihydroxyazo dyes have markedly greater stability to mineral acids and alkalis than the corresponding copper derivatives.[18] The special properties of the chromium complexes of *o,o′*-dihydroxyazo dyes fully explain why chromium is the preferred metal for mordanting acid dyes on wool and why the dyes which lead to the greatest improvement in fastness by chroming possess two hydroxyl groups, both *ortho* to the azo group.

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[16] See Chapter XI for a discussion of azophenol-quinonehydrazone tautomerism.

[2] See p. 551.

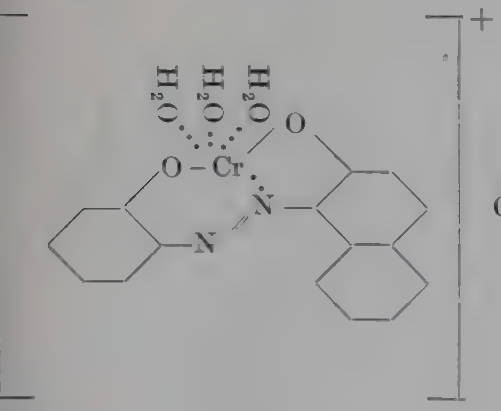
[9] See p. 555.

[17] See also Singu, *Nature* **143,** 1068 (1939).

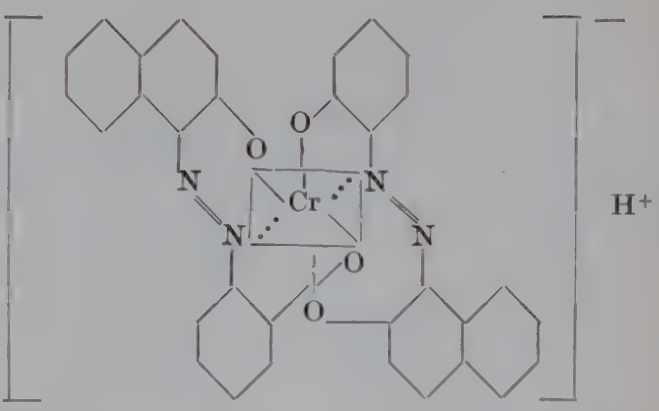
[18] Drew and Fairbairn, *JCS* 823 (**1939**).

Treatment of *o*-hydroxybenzeneazo-β-naphthol with chromium chloride in alcohol gives first the dark purple crystalline compound (I), in which the plane of the azo dye residue is perpendicular to that of the three addenda (e.g., $3H_2O$) coordinated with the chromium atom. The substance is soluble in water, but by prolonged boiling with water, or by heating, the water molecules of crystallization and of coordination are progressively lost, with formation of an insoluble compound, still containing chlorine, but not ionizable.[18]

If (I) is treated with a second molecule of the azo dye, the complex (II) is obtained; (II) is a monobasic acid, insoluble in water, but soluble in alkali. If (II) contained two sulfonic groups, it would be a tribasic acid. Drew and Fairbairn suggest that in (II) and similar complexes it seems stereochemically possible that the negatively charged chromium atom can still maintain octahedral symmetry, the median planes of the two azo residues being inclined perpendicularly to one another as indicated.



(I)



(II)

The terms primary and secondary chromium complexes are sometimes employed for distinguishing between the complexes which contain one and two moles respectively of an *o,o′*-dihydroxyazo dye per chromium atom;[18] but a given azo dye may give the primary or the secondary complex first, according to the conditions under which the complex is prepared.

The azo dye (2-aminophenol-4-sulfonic acid ⟶ β-naphthol) forms a complex that crystallizes in lustrous dark purple needles and probably is a zwitterion (III). The complex (III) is soluble in water. Treatment of (III) with oxalic acid removes the chromium and the original dye is recovered unchanged. No oxidation has occurred during complex formation. Condensation of (III) with a second mole of the azo dye gives a purple-black complex which is analogous to (II) and is a tribasic acid.

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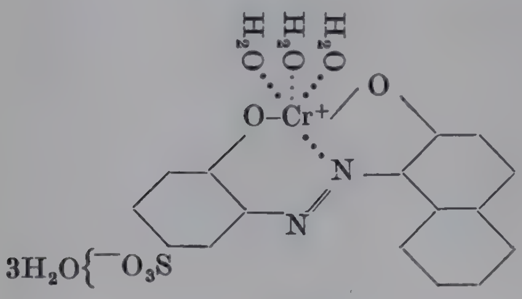
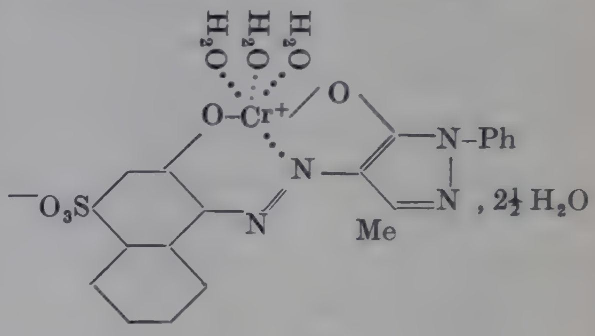
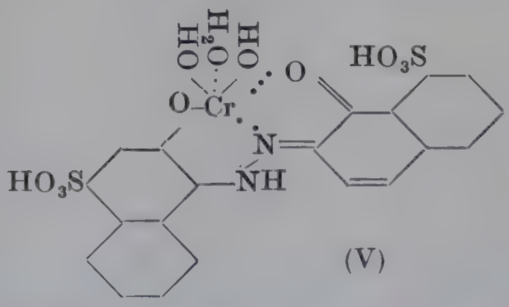
[18] See p. 560.

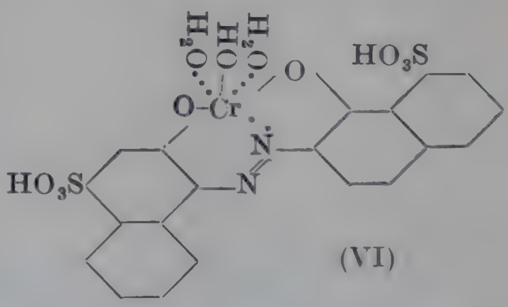

(III)


(IV)

The azo dye (1-amino-2-naphthol-4-sulfonic acid⟶1-phenyl-3-methyl-5-pyrazolone) (Eriochrome Red B) gives with chromium chloride in alcohol a red crystalline complex of the constitution (IV).[18, 19]

The soluble coordination complexes, such as the Palatine Fast and Neolan colors apparently have one metal atom per dye molecule; and Valko has formulated Palatine Fast Blue GGN as (V).[20] The grounds for assigning a hydrazone structure have not been stated, and the azo constitution (VI) is not invalidated. During the dyeing process, it is probable that the coordinated water molecules or the covalently linked hydroxyl group are replaced by carboxyl, amino or amide groups in the wool molecule.


(V)


(VI)

Although Morgan and Main Smith[6, 7] assigned to the cobaltic and chromic complexes of dyes such as Eriochrome Red B and Eriochrome Blue Black R (1-amino-2-naphthol-4-sulfonic acid⟶β-naphthol) structures in which only one hydroxyl group takes part in the chelation of the metal atom, they realized the great dissimilarity between *o*-hydroxy- and *o,o'*-dihydroxyazo dyes in their ability to form stable coordination complexes; but the alternative oxadiazoline structures suggested by them to account

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[18] See p. 560.

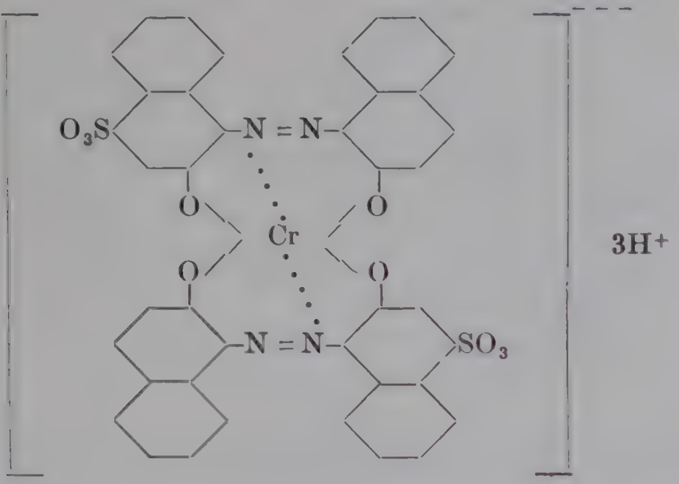
[19] Contrast Morgan and Main Smith, ref. 6.

[20] *Oesterr. Chem. Ztg.* **40**, 465 (1937); Kolloid Chemische Grundlagen der Textilveredlung, Springer, Berlin, 1937.

[6] See p. 553.

[7] See p. 554.

for the part played by the two hydroxyl groups are untenable for several reasons. The complexes described by them need to be reinvestigated in the light of Drew's much more careful experimental work. The chromium complex of Eriochrome Blue Black R probably has the constitution (VII).[21]



(VII)

All the above complexes contain two hydroxyl groups *ortho* to the azo group; one can be replaced by COOH without a change in the character of the complex.[18]

Aluminium and vanadium lakes. Aluminium salts form complexes with *o,o′*-dihydroxyazo dyes, which are similar in structure to the chromium lakes, but much less stable to acids. Technically, interest in aluminium as a mordant is limited to alizarin (see Chapter XXVIII). Vanadium salts yield two series of complexes: vanadyl compounds similar in structure to the principal complexes of tervalent chromium, and vanadi-complexes in which the metal exerts its full quadrivalency in combination with two residues of the azo dye.[22] The coordination number of quadrivalent vanadium is six.

OXIDIZABLE *o*-HYDROXY AND *o,o′*-DIHYDROXYAZO DYES

While many *o,o′*-dihydroxyazo dyes form lakes normally, some undergo oxidation to quinonoid forms, and the latter are involved in the complex formation. Diamond Black PV (2-aminophenol-4-sulfonic acid ⟶ 1,5-dihydroxynaphthalene) forms with chromium fluoride a complex in which, according to Morgan and Main Smith,[6, 7] an azo nitrogen and one of the hydroxyl groups take part in the chelation; the dye molecule thus remains in its original unoxidized condition, and the shade on wool is then a dark purple. This complex, however, is undoubtedly to be represented by a structure in which both the *o*-hydroxyls are implicated in the complex formation; but the analytical data will have to be reexamined. On afterchroming with dichromate and acid in proportions corresponding to 12 equivalents of oxygen, the shade develops to a full black. By analogy with Morgan and Main Smith's formulation for the corresponding cobalt complex, the chromium complex possesses the structure (I) in which the azo group is no longer implicated in the chelate group which is formed by oxidation of the dihydroxynaphthalene to a 5-hydroxy-1,4-naphthoquinone derivative.[23] In considering the possible constitutional formulas for the chromium complex of Diamond Black PV produced on the fiber, it is necessary to remember the outstanding fastness properties of the shade, especially to potting. Morgan and Main Smith provide analytical data for the cobalt complex of the oxidized dye, but not of the chromium complex. The structure (I) for the chromium complex of Diamond Black PV after oxidation does not distinguish it from the corresponding chromium complex of the Chromotropes to which, according to Morgan and Main Smith's ideas, the structure (II) should be assigned. A significant difference between the two parent azo dyes is that Diamond Black PV has hydroxyl groups in both the *o*- and *o′*-positions to the azo group, while the Chromotropes have only one *o*-hydroxyl group. This is doubtless concerned in the greater stability of the Diamond Black complex, and structures in which the two hydroxyl groups as well as the azo and the quinone groups are involved in the formation of the metal chelate merit consideration. The absorption spectra of the complexes from a Chromotrope, Diamond Black PV (unoxidized and oxidized) and Naphthazarin should provide useful data.

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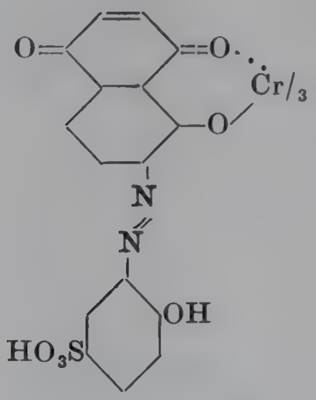
[21] Royer, Millson and Amick, *J. Soc. Dyers Colourists* **63**, 217 (1947).

[18] See p. 560.

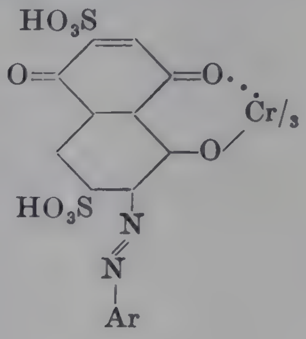
[22] Drew and Dunton, *JCS* 1064 (**1940**).

[6] See p. 553.

[7] See p. 554.



(I)



(II)

Carmoisine WS (III) shows no signs of complex formation with either chromium fluoride or roseocobaltic chloride;[7] with chromic acid the shade changes from red through purple to blue-black, and it is evident that in the case of such monohydroxyazo dyes the formation of metallic complexes occurs only after oxidation. The constituton of such lakes has not been adequately investigated. Rosenhauer, Wirth and Königer[24] consider

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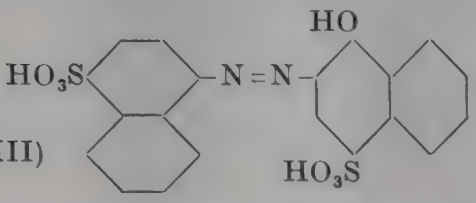
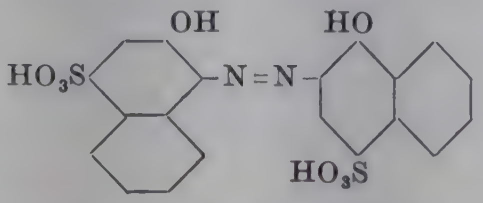
[23] See also Burstall, *J. Oil Color Chem. Assoc.* **20**, 186 (1937).

[7] See p. 554.



(III)

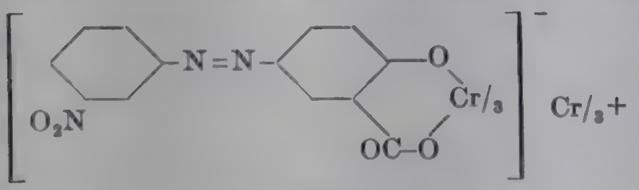


(IV)

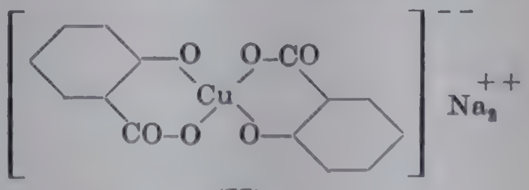
the blue-black oxidation lake of Carmoisine WS to be identical with the chromium lake derived from the interaction of chromic salts and Eriochrome Blue Black B; they suggest that in the case of Carmoisine WS it is only after the conversion of the mono-*o*-hydroxyazo dye into an *o,o'*-dihydroxy dye (IV) by chromic acid that a chromium complex can be formed. The nuclear hydroxylation of a naphthalene to a β-naphthol derivative appears to be very improbable. Further, it has been mentioned that Eriochrome Blue Black B is prepared from α-naphthol as second component, and it is obvious that the mechanism of the action of dichromate on Carmoisine WS needs further investigation.

AZOSALICYLIC ACIDS

Chromium compounds. The chromic complex of Alizarin Yellow 2G (*m*-nitroaniline⟶salicylic acid) has the constitution (I) in which chromium is implicated in the chelate complex and is also present as chromic salt.[7] The azo groups do not take part in the complex formation, since coordination of the metal with azo-nitrogen is not possible when the metallic atom is in combination with the hydroxyl and carboxyl groups; it has been mentioned earlier that the azo group enters into coordination with a metal only when both are implicated in a chelate ring. The ability of certain hydroxy acids to form metallic complexes is well known; the complexes are more stable the stronger the acidity of the hydroxyl group, and salicylic acid gives stable crystalline complexes of type (II).[25] The fact that the chromophoric azo group is not involved in the formation of the metallic complex explains why the azosalicylic acid dyes change much less in color by afterchroming (or other mordanting) than the *o,o'*-dihydroxyazo dyes.



(I)



(II)

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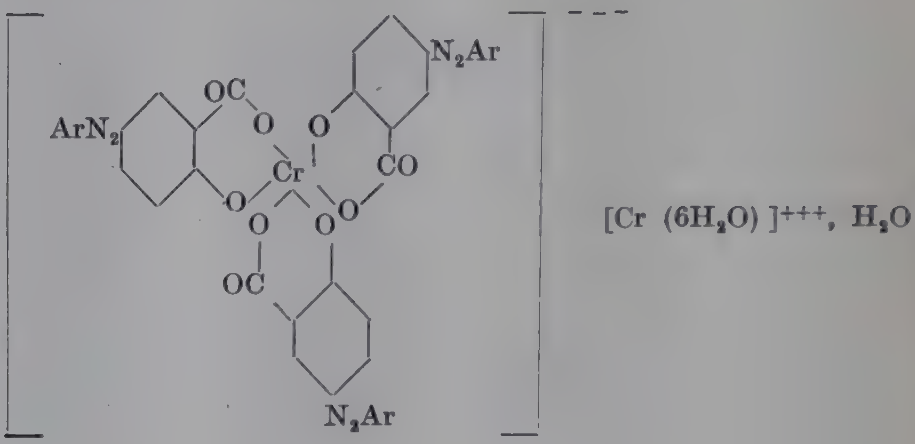
[24] *Ber.* **62**, 2717 (1929).

[7] See p. 554.

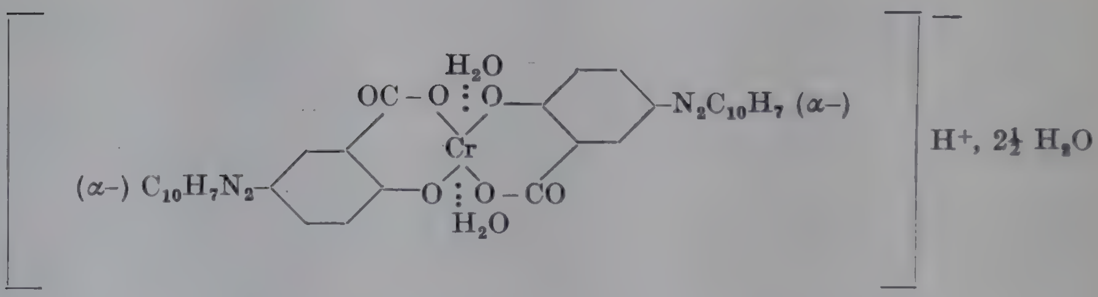
[25] Wark, *JCS* **123**, 1815 (1923); 1753 (1927).

Drew and Fairbairn have isolated two main types of azosalicylic acid complexes; one in which two chromium atoms are in combination with three molecules of the azosalicylic acid (III) is of the same type as the complex (I) prepared earlier by Morgan and Main Smith; the other (IV) is a monobasic acid with chromium and azosalicylic acid in the proportion 1,2. The complex (III) may be regarded as belonging to Type (4) or (7)

(III)



(IV)



among the types of chromic compounds mentioned on p. 552; and the complex (IV) to Type (3) or Type (5). In these salicylic acid derivatives, the two types mentioned for each compound are in fact equivalent because of the resonance of the carboxyl group.

Copper compounds. Copper behaves like chromium in its mode of combination with the azosalicylic acids; the metal does not coordinate with azo-nitrogen, and the complex is formed by the attachment of the metal to the carboxyl and *o*-hydroxyl groups. Thus benzeneazo-*o*-cresotinic acid forms with alcoholic copper acetate the brown cupri-complex dihydrate (V).[18]

Mordant Yellow O (2-naphthylamine-6-sulfonic acid⟶salicylic acid) gives simple salts with copper, nickel and cobalt salts, the metals being replaceable by barium. With coordinated ammines, such as cuprammonium sulfate and aquopentammine cobaltic chloride, the inner complexes are formed. The copper lake appears to have the constitution (VI); on drying, one molecule of ammonia and two of water are lost. The two molecules of water return on keeping the substance in air.[26]

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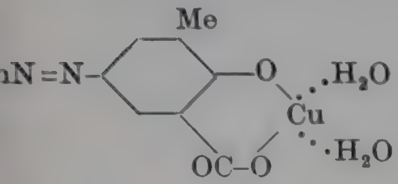
[18] See p. 560.



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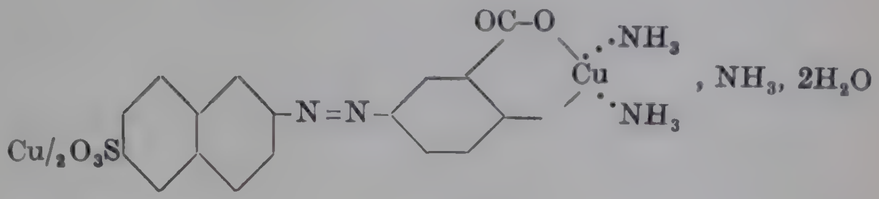
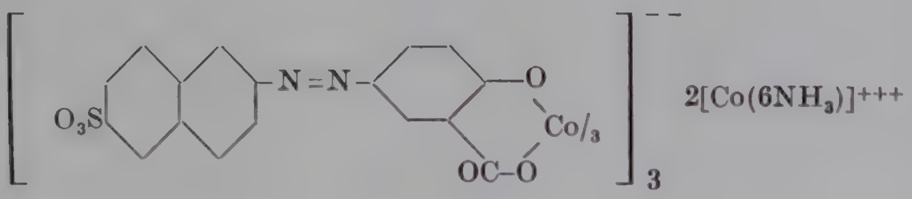
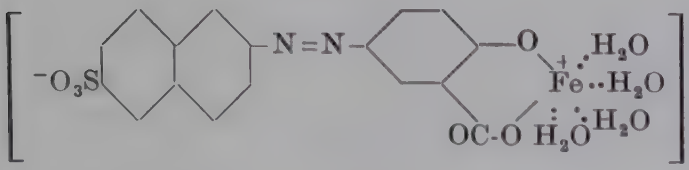


(VI)

Cobalt and iron compounds. The cobaltammine complex of Mordant Yellow O has the structure (VII). Ferric chloride yields the complex (VIII).[26]



(VII)



(VIII)

THE METAL-DYE-PROTEIN COMPLEX

The literature on the mechanism of the mordanting of animal fibers has been surveyed by Giles.[27] Chromium mordants are dealt with extensively, and the nature of the compounds present on the fiber, both before and after dyeing, is discussed. Wool is usually mordanted with sodium or potassium dichromate, with the addition if necessary of acetic acid or an organic acidic reducing agent such as oxalic and tartaric acid. The fiber absorbs chromic acid, and at the high temperature of the dyeing process the chromic acid undergoes reduction by means of the sulfur in the cystine component of the fibrous protein, and compounds are formed in which chromium is the cation. The dyed fiber contains chromium atoms linked with both dye and wool molecules.

The constitution of the dye-chromium complexes formed when wool is dyed with (I), (II) and Metachrome Brilliant Blue BL (III) by the onchrome, metachrome, and afterchrome processes has been established.[28]

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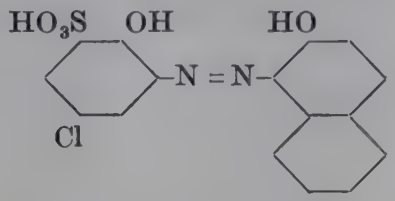
[26] Kudva, unpublished work.

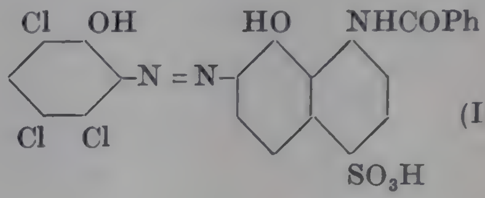
[27] *J. Soc. Dyers Colourists* **60**, 303 (1944).

[28] Race, Rowe and Speakman, *J. Soc. Dyers Colourists* **62**, 372 (1946).

The technique employed was to remove excess chromium from the wool by continuous extraction with oxalic acid solution at room temperature, and relate the residual chromium to the dye on the fiber quantitatively. In the case of (II) and (III) the complex, probably a tribasic acid, consists of two molecules of dye and one atom of chromium, regardless of the dyeing method. The complex is similarly constituted when (I) is applied by the onchrome or afterchrome processes, but by the metachrome process a true dye lake is not formed or is unstable to oxalic acid. The complex formed on the fiber is in effect an acid dye of high molecular weight, and the increased fastness of the chromed dyeings in comparison with the unchromed dyeings may be attributed to the fact that the complex is bound to the fiber by van der Waals forces commensurate with its size, and to the possibility that the molecules of the complex, having been formed *in situ*, are too large to escape from spaces large enough to allow initial entry of individual dye molecules and chromium ions.[28]

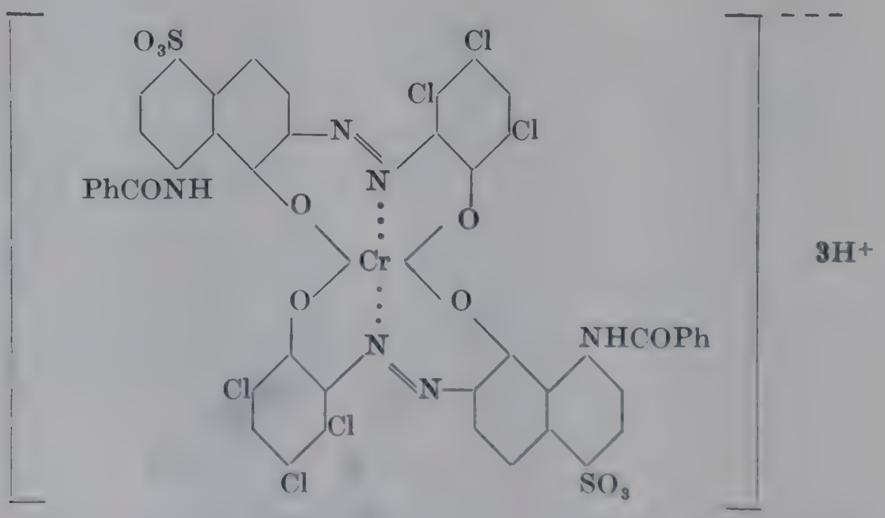
(I)





(II)

In the normal chroming methods, chromium is used in great excess, and much brighter shades are obtained if chromium is used in stoichiometric proportion for the formation of the 2:1 dye-chromium complex. The complexes can be prepared in substance, and they dye similar shades as in dyeing when the dye and chromium are applied to the fiber in the required proportions for the 2:1 complex. This complex is probably a tribasic acid,



(IV)

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[28] See p. 567.

constituted as (IV) in the case of dye (II). Since the only charges associated with the 2:1 complex are the anionic valencies of chromium and sulfonic groups, the complex and fiber appear to combine by means of salt linkages between chromium and sulfonic groups in the complex and amino groups in the fiber.[28]

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[28] See p. 567.

CHAPTER XV

TRISAZO AND POLYKISAZO DYES[1-6]

TRISAZO DYES

Trisazo dyes in general are direct cotton dyes, while a few are useful for leather. The shades vary from brown, through blue and green, to black. The synthesis of dyes containing three azo groups may be effected by five main methods.

1. Using a tetrazotized diamine, such as benzidine, the coupling of the two diazo groups and the introduction of the third azo unit can be carried out by several variations of the main scheme: (*a*) A benzidine type of disazo dye containing a diazotizable amino group is diazotized and coupled with an end component. The whole scheme of preparation therefore is ($E^1 \longleftarrow D \longrightarrow M \longrightarrow E^2$). (*b*) A diamine is tetrazotized and coupled with one mole of a primary amine unsubstituted in the *p*-position, the amino group is then diazotized, and the *bis*-diazonium salt is coupled with two moles of an end component ($E \xleftarrow{2} M \xleftarrow{1} D \xrightarrow{2} E$). (*c*) A tetrazotized diamine is coupled with one mole of a monoazo compound and with one mole of another component ($\mathrm{Ar{-}N{=}N{-}Ar'} \xleftarrow{1} D \xrightarrow{2} E$). The entire scheme may therefore be written as ($A \xrightarrow{1} Z \xleftarrow{3 \text{ or } 2} D \xrightarrow{2 \text{ or } 3} E$). The order of the two couplings of the tetrazotized diamine may be reversed, depending on the relative ease of coupling of the two second components (E and the monoazo dye from Z). (*d*) A tetrazotized diamine is coupled with one mole of a normal second component with one coupling position, and one mole of a second component with two coupling positions; the disazo dye is then coupled with a new diazonium component ($E \xleftarrow{1} D \xrightarrow{2} Z \xleftarrow{3} A$). (*e*) A tetrazotized diamine is coupled with one mole of a second component with two coupling positions; the second position in the latter is then coupled with a diazonium salt, and finally the second diazonium radical in the tetrazotized diamine is coupled with an end component ($A \xrightarrow{2} Z \xleftarrow{1} D \xrightarrow{3} E$).

2. The coupling of a diazonium salt with a primary aromatic amine in the *p*-position or an aminonaphthol such as γ-acid under alkaline conditions, so that a diazotizable amino group is available, is repeated twice, and the amino-disazo dye is then diazotized and coupled with an end component ($A \longrightarrow M^1 \longrightarrow M^2 \longrightarrow E$).

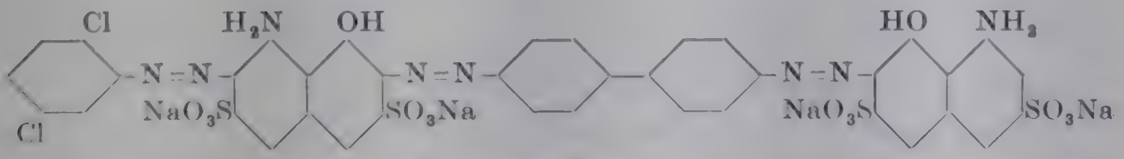
[1-6] As in Chapter XII.

3. A diazotized aminoazo compound and an aryldiazonium salt are coupled with a dual coupling component ($A^1 \longrightarrow M \longrightarrow Z \longleftarrow A^2$).

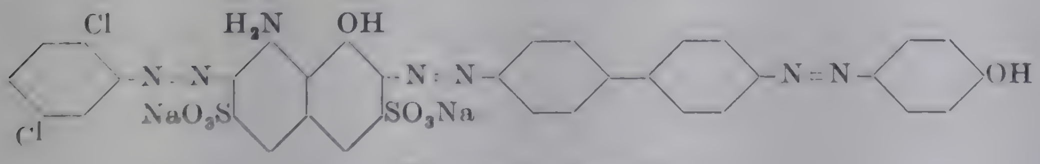
4. A second component with three coupling positions, such as *m*-phenylenediamine and resorcinol, is coupled thrice with three moles of the same or different diazonium salts [$A^1 \longrightarrow \underset{\substack{\uparrow \\ A^3}}{T} \longleftarrow A^2$].

5. Methods using phosgene or cyanuric chloride.

Trisazo dyes derived from benzidine. The direct cotton dye, Triazol Orange B (GrE) (4-nitroaniline-2-sulfonic acid $\xrightarrow{1.\ \text{acid}}$ J-acid $\xleftarrow{3.\ \text{alk.}}$ benzidine $\xrightarrow{2}$ salicylic acid) is an interesting example of an orange trisazo dye.[6] Benzo Fast Blue R (Schultz, 1890) (By; CI 567) (ε-acid $\xleftarrow{2}$ *o*-tolidine $\xrightarrow{1}$ α-naphthylamine $\xrightarrow{2}$ ε-acid) has good light fastness. The analog from dianisidine is a purer blue, Benzo Fast Blue B (By; CI 576). Diamine Steel Blue LCC (4-nitro-*o*-toluidine $\xrightarrow{1.\ \text{acid}}$ H-acid $\xleftarrow{2.\ \text{alk.}}$ *o*-tolidine $\xrightarrow{3.\ \text{alk}}$ S-acid+Chicago acid) and Triazol Dark Blue B (GrE) (H-acid $\xleftarrow{2.\ \text{alk.}}$ benzidine $\xrightarrow{3.\ \text{alk.}}$ J-acid $\xleftarrow{1.\ \text{acid}}$ 4-nitroaniline-2-sulfonic acid) have poor light fastness (2).[6] The color of Chloramine Blue 3G (S; CI 590) (2,5-dichloroaniline $\xrightarrow{1.\ \text{acid}}$ H-acid $\xleftarrow{2.\ \text{alk.}}$ benzidine $\xrightarrow{3.\ \text{alk.}}$ H-acid) is of interest in comparison with that of Chloramine Green B. Among the trisazo dyes of this type, there are several greens. Erie Green WT (NAC; CI 583) (Benzo Dark Green B; IG) (aniline $\xrightarrow{2.\ \text{alk.}}$ H-acid $\xleftarrow{1.\ \text{acid}}$ benzidine $\xrightarrow{3}$ phenol) has light fastness 2–3, slightly improved by aftertreatment with chromium fluoride.[6, 7] Chloramine Green B (Böniger and Lagutt, 1898) (S; CI 589) is (2,5-dichloroaniline $\xrightarrow{1.\ \text{acid}}$ H-acid $\xleftarrow{3.\ \text{alk.}}$ benzidine $\xrightarrow{2}$ phenol) is a brighter and purer green; Diamine Green CL (IG) is similarly constituted, *o*-chloroaniline taking the place of dichloroaniline. An important member of this series of trisazo greens is Diamine Green B (Hoffmann and Daimler, 1891)



Chloramine Blue 3G



Chloramine Green B

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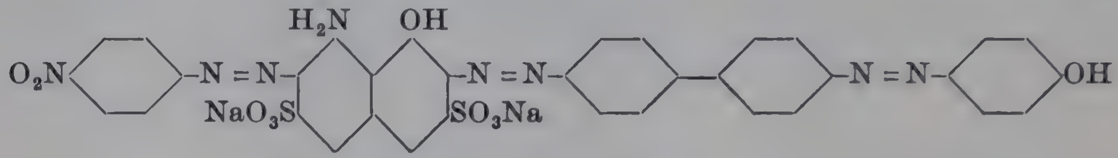
[6] See p. 570.

[7] See Chapter XVII.

(CI 593), which was the first green direct cotton color and which continues to be used extensively on cotton, wool and union fabrics. It is constituted similarly to Chloramine Green B; the acid coupling of H-acid is carried out with *p*-nitroaniline in place of dichloroaniline.[2] Other green dyes in the series are Benzo Dark Green GG (By) (α-naphthylamine$\xrightarrow{2}$H-acid $\xleftarrow{1.\ \text{acid}}$benzidine$\xrightarrow{3}$phenol); and Benzo Green FF (By) (aniline-2,5-disulfonic acid$\xrightarrow{1.\ \text{acid}}$S-acid$\xleftarrow{3}$*o*-tolidine$\xrightarrow{2}$salicylic acid). Benzo Olive (By) has been stated to be (salicylic acid←benzidine→α-naphthylamine $\xrightarrow{\text{alk.}}$H-acid; CI 558) and (salicylic acid←benzidine→Cleve-7-acid→ dioxy-S-acid).[6]



Diamine Green B

A series of brown trisazo dyes are made by schemes involving the use of benzidine. Examples[2, 6] are: Benzo Chrome Brown B (By) (salicylic acid$\xleftarrow{1}$benzidine$\xrightarrow{2}$Cleve-7-acid$\xrightarrow{3}$Cleve-6-acid); Columbia Bronze B (IG) (salicylic acid$\xleftarrow{1}$benzidine$\xrightarrow{2}$Cleve acids$\xrightarrow{3}$γ-acid); Benzo Dark Brown extra (salicylic acid←benzidine→Cleve acids→Laurent acid); Naphthamine Brown 4G extra (salicylic acid←benzidine→resorcinol ←metanilic acid); Oxydiamine Brown G (*m*-toluylenediamine-5-sulfonic acid←benzidine→*m*-phenylenediamine←sulfanilic acid); Oxamine Brown B and Columbia Catechin R (salicylic acid←benzidine→*m*-phenylenediamine←aniline-2,4-disulfonic acid or 2R-acid); Oxamine Brown GX and GRX (1-chloro-2,6-diaminobenzene-4-sulfonic acid← benzidine→*m*-toluylenediamine←sulfanilic or naphthionic acid); Columbia Brown R (γ-acid←benzidine→*m*-toluylenediamine←sulfanilic acid). Examples of browns prepared by somewhat similar methods, but using *m*- or *p*-phenylenediamine derivatives, are Toluylene Brown T or 3M (*m*-phenylenediamine←2,6-toluylenediamine-4-sulfonic acid→ *m*-phenylenediamine←naphthionic acid); Oxamine Dark Brown BG (*p*-aminoacetanilide→NW-acid; saponify;→Cleve acid→J-acid); Naphthamine Direct Brown V (2-*p*-aminobenzeneazonaphthionic acid→*m*-phenylenediamine←metanilic acid).

Direct Deep Black EW extra (Kahn, 1898) (By; CI 581) (Direct Black E) (aniline$\xrightarrow{2}$H-acid$\xleftarrow{1}$benzidine$\xrightarrow{3}$*m*-phenylenediamine) is a common black dye for cotton, union fabrics, and leather, and the IG production of Direct Black E has been stated to be two million kilograms per year. It can be aftertreated on the fiber with formaldehyde or with a diazonium salt (e.g., diazotized *p*-nitroaniline), the washing fastness being thus increased; the light fastness, however, is only 2–3. A dye with slightly higher light fastness is Diamine Black HW (Hoffmann and Daimler, 1891) (C; CI 592) (*p*-nitroaniline $\xrightarrow{1}$ H-acid $\xleftarrow{2}$ benzidine $\xrightarrow{3}$ γ-acid).[2] Useful dyes (IG) for leather such as Chrome Fast Leather Black V (sulfanilic acid $\xrightarrow{\text{acid}}$ H-acid ← mixed benzidine-tolidine → 2,4-dihydroxyquinoline) and Chrome Fast Leather Black S (sulfanilic acid $\xrightarrow{\text{acid}}$ H-acid ← benzidine → *m*-acetamidodiethylaniline) are prepared by similar schemes.[6]

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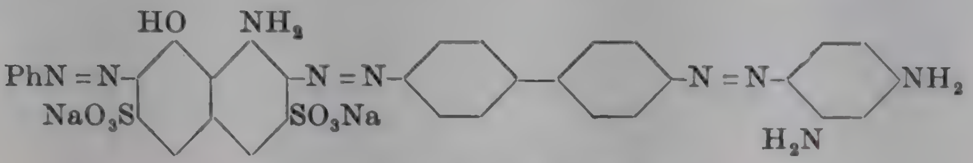
[2] See p. 570.

[6] See p. 570.



Direct Deep Black EW extra

Trisazo dyes **(A → M^1 → M^2 → E).** A series of important blue, green, brown, and gray direct cotton dyes with very good fastness to light (5–6) are prepared by the scheme (A → M^1 → M^2 → E) in which E is J-acid, phenyl-J-acid or *N*-benzoyl-J-acid; M^1 and M^2 are α-naphthylamine, Cleve acids, 2-ethoxy-1-naphthylamine or its 6-sulfonic acid. Several of the Benzo Fast dyes (By) and Sirius dyes (IG) belong to this type. The aminodisazo dye obtained at the second stage undergoes normal diazotization; but in some cases the diazonium salt is very weak in its coupling power, and the final coupling has to be carried out by replacing the usual aqueous alkaline bath by a pyridine-ammonia medium. The monoazo dyes (A → 2-ethoxy-1-naphthylamine), their diazonium salts, and the disazo dyes (A → 2-ethoxy-1-naphthylamine → E) are notable for their instability.[8]

Benzo Fast Blue FR (CI 533)(aniline → Cleve-6-acid → Cleve-6-acid $\xrightarrow{\text{alk.}}$ J-acid) is a level-dyeing dye. Sirius Blue GR is similarly constituted (aniline-2,5-disulfonic acid → Cleve-7-acid → α-naphthylamine → J-acid).[6] Sirius Supra Blue BRR, which has light fastness 6, employs naphthalene derivatives for all the four components (2-naphthylamine-4,8-disulfonic acid → α-naphthylamine → Cleve-7-acid → J-acid).[2] A series of blue dyes of this type are prepared by using phenyl-J-acid (I) as E. Examples[2, 9] are Benzo Fast Blue FFB (metanilic acid → α-naphthylamine → Cleve-6-acid → I); Sirius Supra Blue G (aniline-2,5-disulfonic acid → Cleve-7-acid → α-naphthylamine → I); and Benzo Fast Blue 2GL (aniline-2,5-disulfonic acid → α-naphthylamine → Cleve-7-acid → I). The difference in the structures of these dyes is only in the number and position of the sulfonic groups. A closely related dye, bright greenish blue in shade, in which M^2 is 2-ethoxy-Cleve acid, is Sirius Supra Blue 6G (Schweitzer, 1924).[6, 10, 11] Sirius Supra Blue BR is (2-naphthylamine-4,8-disulfonic acid⟶α-naphthylamine⟶Cleve-7-acid⟶I).[6] For Sirius Blue FG phenyl-γ-acid is the end component: (aniline-2,5-disulfonic acid⟶α-naphthylamine⟶Cleve-6-acid⟶phenyl-γ-acid).[5]

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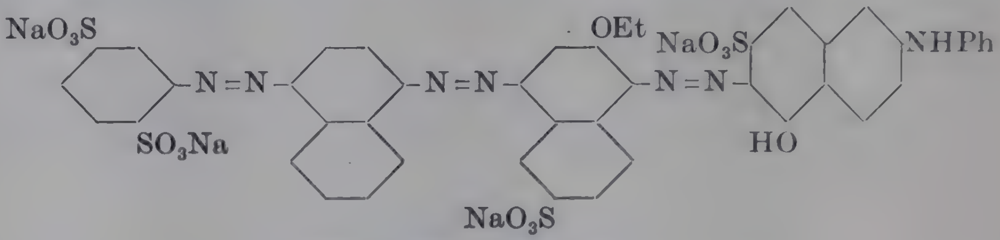
[2] See p. 570.

[6] See p. 570.

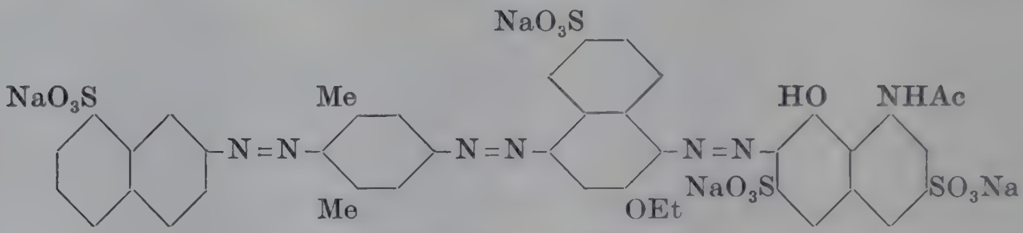
[8] Fierz-David *et al.*, *Helv. Chim. Acta* **21**, 664, 1367 (1938).

[9] Fierz-David, Künstliche Organische Farbstoffe, Springer, Berlin, 1926.



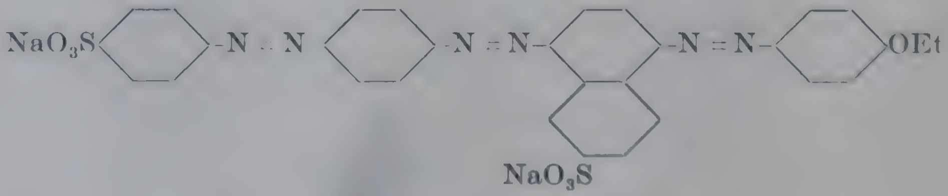
Sirius Supra Blue 6G

Using acetyl-H-acid for E, the useful green dye, Sirius Supra Green BB, is obtained;[2] it dyes a bright bluish green with good fastness to light (5–6) and moderate fastness to washing (2–3).



Sirius Supra Green BB

Brown and gray dyes with high light fastness have also been prepared by the scheme ($A\longrightarrow M^1\longrightarrow M^2\longrightarrow E$). Sirius Brown RV (2-naphthylamine-4,8-disulfonic acid⟶α-naphthylamine⟶cresidine⟶4-nitro-*m*-phenylenediamine) has good fastness to light (5), but poor fastness to water and washing.[2] Toluylene Fast Brown 3G is a similar dye with slightly inferior light fastness (4), in which M^1 and M^2 are *m*-toluidine and *o*-toluidine respectively.[2] Sirius Supra Brown RL (sulfanilic acid⟶aniline⟶Cleve-6-acid⟶phenol; ethylate) is bright and level dyeing, and is recommended for viscose-cellulose acetate stockings in which the acetate rayon is left



Sirius Supra Brown RL

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[6] See p. 570.

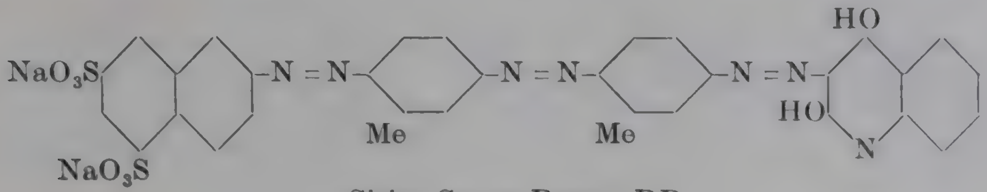
[10] *Ibid.*, Ergänzungsband, 1935.

[11] Rowe, The Development of the Chemistry of Commercial Dyes, Institute of Chemistry, London, 1938.

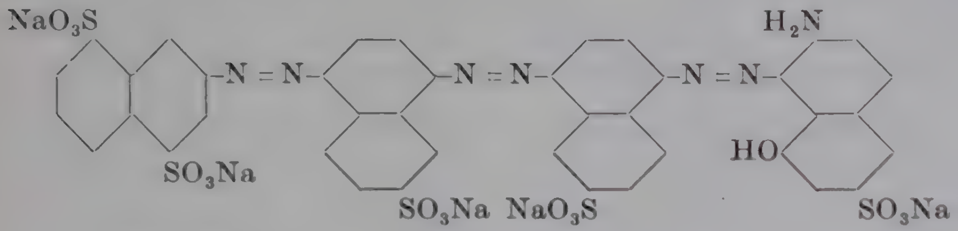
[5] See p. 570.

[2] See p. 570.

undyed. Sirius Supra Brown RD has excellent discharge properties.[12] γ-Acid (acid coupled) as E yields gray dyes and examples are: Sirius Gray RR (aniline $\longrightarrow$ Cleve acids $\longrightarrow$ Cleve acids $\xrightarrow{\text{acid}}$ γ-acid); Benzo Fast Gray BL (By, 1914) (2-naphthylamine-4,8-disulfonic acid $\longrightarrow$ α-naphthylamine $\longrightarrow$ Cleve-7-acid $\xrightarrow{\text{acid}}$ γ-acid); and Sirius Gray G.[5, 6] "Surprising fastness to boiling" is claimed for the gray trisazo dye (2,6-dichloro-*p*-nitroaniline $\longrightarrow$ Cleve-7-acid $\longrightarrow$ Cleve-7-acid $\longrightarrow$ J-acid).[13]

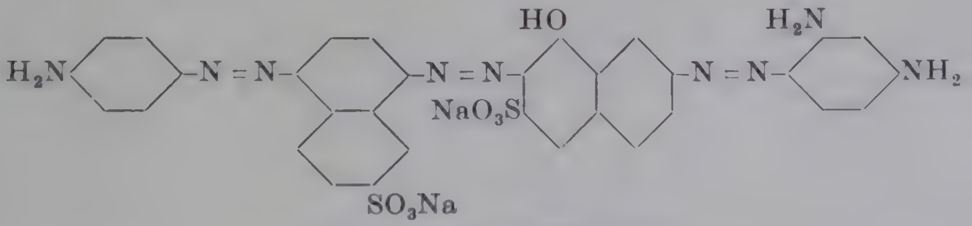


Sirius Supra Brown RD



Sirius Grey G

Miscellaneous trisazo dyes. Columbia Black FF extra (AGFA; Clausius and Seidel, 1898) is an important black dye, which has good fastness to perspiration and is largely used for dyeing lining material.[14]



Columbia Black FF extra

Di-J-acid is a useful intermediate for the preparation of trisazo dyes by the scheme ($A^1 \xrightarrow{1} M \xrightarrow{2} Z \xleftarrow{3} A^2$). If the dye contains a salicylic acid residue, it becomes suitable for aftertreatment with copper.[7] Blue trisazo dyes for cotton, suitable for aftercoppering, are prepared by the scheme (aminosalicylic acid $\longrightarrow$ 2,5-dialkoxyaniline $\longrightarrow$ di-J-acid $\longleftarrow$ 2,5-dialkoxyaniline). Tris- or polyazo dyes for cotton in which the end component favoring substantivity is 8-hydroxyquinoline, and which may contain further lake-forming groups for metallization on the fiber, have been described.[15]

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[12] *FIAT* 1313, III; for further examples of tetra-, penta-, and hexakisazo dyes for cotton, derived from H-acid, see Geigy, SP 248,689-96; USP 2,488,076.

[5] See p. 570.

[6] See p. 570.

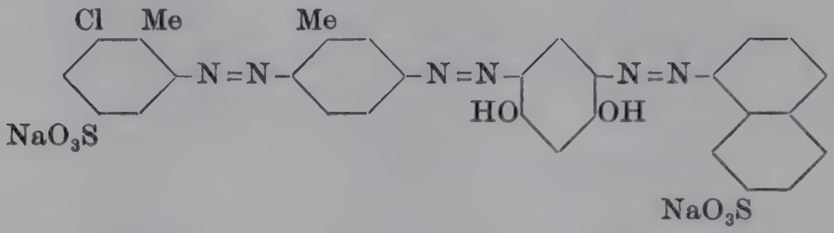
[13] Ciba, BP 589,329; see also SP 244,770-5.

[14] See Chapter XI.

[7] See p. 571.

[15] Ciba, BP 533,364.

6-Chloro-*o*-toluidine-4-sulfonic acid as the first component appears to impart desirable properties to leather dyes, such as Acid Leather Brown EGR.[1]



Acid Leather Brown EGR

Brown trisazo dyes for leather are obtained by coupling resorcinol successively with one mole each of diazotized (*a*) 5-aminosalicylic acid; (*b*) picramic acid; and (*c*) *p*-nitroaniline. The trisazo dye obtained by coupling resorcinol successively with diazotized H-acid and two moles of diazotized 4-nitro-2-aminophenol forms chromium and copper complexes which give fast level shades on leather.[16] In such cases it is unlikely that the third coupling on resorcinol proceeds to completion, and there is the possibility that the third molecule of diazonium salt couples with the salicylic or H-acid residue.

TETRAKISAZO DYES

Like the trisazo dyes, the tetrakisazo dyes are direct cotton colors, and the shades are mainly restricted to deep browns and blacks. There is little advantage to be gained by introducing more than three azo groups into a dye molecule. With such multiplication of azo groups and a great increase in molecular weight, the colors become darker and less attractive. The solubility and the affinity for textile fibers are sometimes reduced, and tetrakisazo dyes are preferably prepared on the fiber. However, several brown and black dyes containing four and more azo groups are used commercially, while blue and green dyes have been mentioned in patents. A high molecular weight, when the components are suitably chosen, usually means good washing fastness. Difficulties in preparation during the later diazotization and coupling reactions, and loss of brightness in the shades, are encountered in the tetrakisazo dyes in which the azo groups are attached in a linear manner to aromatic ring systems; but when the multiplication of azo groups is effected by phosgenation or cyanuration of the smaller azo dyes, it is possible to secure the advantages of a large molecule without the disadvantages.

Trisulphon Brown B (Böniger, 1897) (S; CI 561) (naphthionic acid $\xrightarrow{1}$ 2R-acid $\xrightarrow{2}$ *m*-toluylenediamine $\xleftarrow{3}$ benzidine $\xrightarrow{3}$ salicylic acid) dyes cotton, aftertreated with dichromate and copper sulfate,[7] chestnut-brown shades with good fastness to light and washing. Replacing benzidine by *o*-tolidine and dianisidine, Trisulphon Brown G (S; CI 570) and GG (CI 577) are obtained. Benzo Brown G (Herzberg, 1887) (By; CI 606) (two moles sulphanilic acid $\Longrightarrow$ Bismarck Brown) is another useful dye. Examples[6] of brown tetrakisazo dyes from the IG range are: Toluylene Brown WR extra and R (2,6-toluylenediamine-4-sulfonic acid $\xRightarrow{1}$ two moles *m*-phenylenediamine or *m*-toluylenediamine $\xLeftarrow{2}$ two moles naphthionic acid); Solamine Brown 4RL (sulfanilic acid $\longrightarrow$ *m*-toluidine $\longrightarrow$ Cleve-6-acid $\longrightarrow$ *m*-toluylenediamine $\longrightarrow$ 4-nitro-*m*-phenylenediamine); and Dianil Brown BD (sulfanilic acid $\xrightarrow{1}$ *m*-phenylenediamine $\xleftarrow{2}$ benzidine-monosulfonic acid $\xrightarrow{3.\ \text{alk.}}$ γ-acid $\xrightarrow{4}$ *m*-phenylenediamine).

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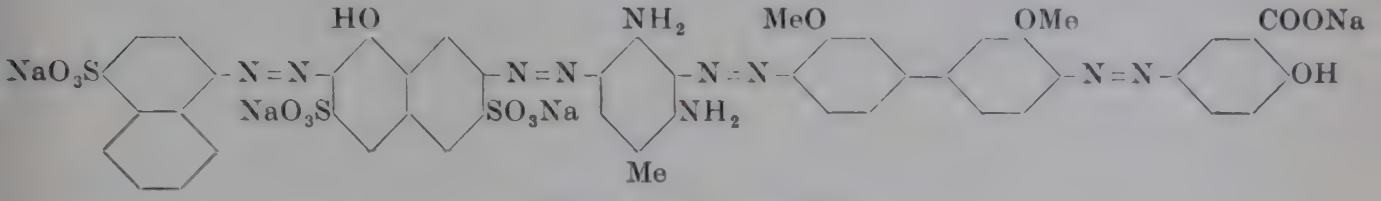
[1] See p. 570.

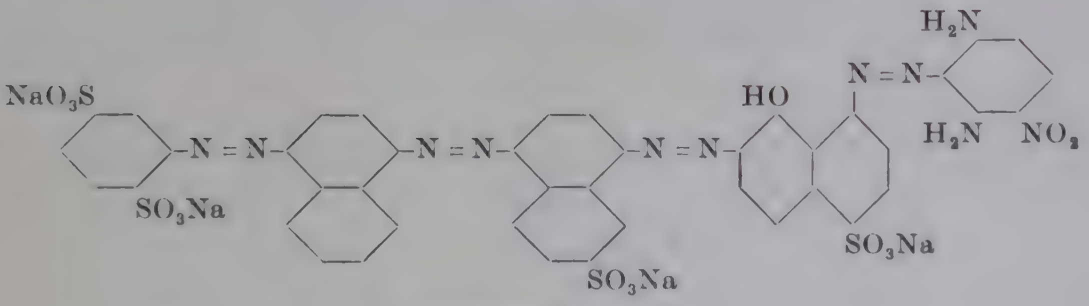
[16] ICI and Mendoza, BP 441,398; IG, BP 496,241.

[7] See p. 571.



Trisulphon Brown GG

Three gray dyes of the Sirius series with light fastness 5–6 are tetrakisazo dyes: Sirius Gray R (2-naphthylamine-4,8-disulfonic acid $\longrightarrow$ α-naphthylamine $\longrightarrow$ Cleve-7-acid $\xrightarrow{\text{alk.}}$ γ-acid $\longrightarrow$ Schaeffer acid); Sirius Gray GB (2-naphthylamine-4,8-disulfonic acid $\longrightarrow$ α-naphthylamine $\longrightarrow$ Cleve-7-acid $\xrightarrow{\text{alk.}}$ S-acid $\longrightarrow$ 4-nitro-*m*-phenylenediamine; and Sirius Supra Gray GG in the preparation of which aniline-2,5-disulfonic acid replaces the naphthylamine disulfonic acid.[5, 6] Naphthamine Fast Black RS (K; CI 619) (2 moles *p*-aminoacetanilide $\Longrightarrow$ H-acid; hydrolyze; $\Longrightarrow$ *m*-phenylenediamine, 2 moles); Oxy Diamine Black T (C) (*m*-phenylenediamine $\longleftarrow$ *o*-tolidine $\xrightarrow{\text{alk.}}$ γ-acid $\longrightarrow$ 2R-acid $\longrightarrow$ *m*-phenylenediamine); and Columbia Black PB (AGFA) (4-nitroaniline-2-sulfonic acid $\xrightarrow{1.\ \text{acid}}$ J-acid $\xleftarrow{3.\ \text{alk.}}$ γ-acid $\xleftarrow{2}$ dianisidine $\xrightarrow{4}$ *m*-phenylenediamine) are among the commercial black



Sirius Supra Gray GG

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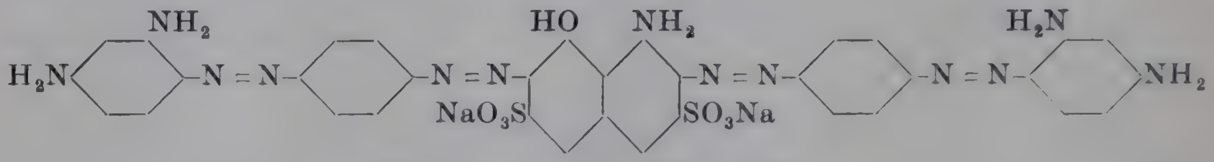
[6] See p. 570.

[5] See p. 570.

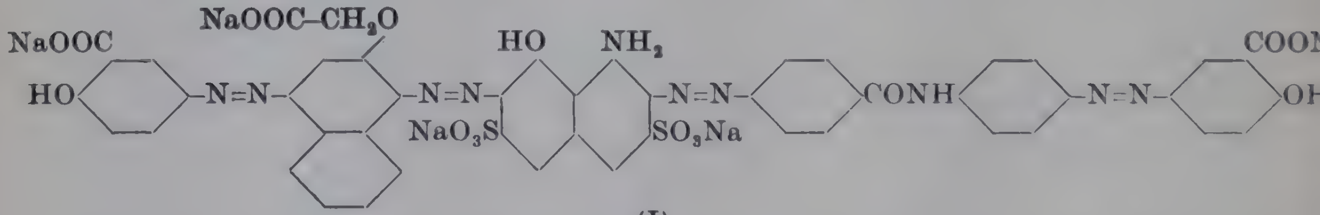
tetrakisazo dyes. Silk Printing Black M (IG) is stated to be (benzidine-3,3′-disulfonic acid $\rightrightarrows$ two moles cresidine $\rightrightarrows$ mixture of one mole 2R-acid and one mole *p*-carboxyphenyl-γ-acid); and Chrome Leather Black A (IG) to be (*p*-aminoacetanilide $\xrightarrow{3}$ H-acid $\xleftarrow{1}$ benzidine $\xrightarrow{2}$ *m*-phenylenediamine $\xleftarrow{4}$ *p*-aminoacetanilide).[6]



Naphthamine Fast Black RS

Yellow to orange tetrakisazo dyes with good affinity for cellulose and fastness to washing are obtained by coupling tetrazotized benzidinedisulfonic acid (or the disulfonic acids of analogous diamines such as diaminostilbene) with two moles of the acetoacetylide of aminoazobenzene.[17]

Useful tetrakisazo dyes for cellulosic fibers with good fastness to washing are obtained by coupling the monoazo dye (anthranilic acid $\xrightarrow{\text{acid}}$ J-acid) with tetrazotized benzidine derivatives in a pyridine-ammonia medium. The dianisidine dye yields marine blue shades, somewhat deepened and rendered faster by aftercoppering.[18] The blue dye (resorcinol ⟵ *p*-phenylenediamine ⟶ Cleve-6-acid ⟶ Cleve-6-acid ⟶ 1-naphthol-3-sulfonic acid) has light fastness 5 and other "excellent properties." The olive green dye (I) has light fastness 5–6.[12] Fast blue-green tetrakisazo dyes are prepared by such a scheme as (metanilic acid $\xrightarrow{1}$ Cleve-7-acid $\xrightarrow{2}$ 2-ethoxy-1-naphthylamine-6-sulfonic acid $\xrightarrow{\text{4. pyridine-ammonia}}$ J-acid $\xleftarrow{\text{3. acid}}$ metanilic acid).[19] A variation, leading to a greener shade of blue and greater fastness to light, is to use 2,5-dimethoxyaniline as a middle component, and orthanilic acid as the diazonium component for the first coupling.[20] Using an aminosalicylic acid in place of one of the metanilic acid molecules, the blue dyes turn a fast gray by coppering.[21] Gray tetrakisazo dyes, such as (5-aminosalicylic acid ⟶ Cleve-6-acid ⟶ cresidine $\xrightarrow{\text{alk.}}$ J-acid $\xleftarrow{\text{acid}}$ 5-chloroanthranilic acid) aftertreated on the fiber with copper or chromium, are fast to light and washing.[2, 22]



(I)

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[6] See p. 570.

[17] Sieglitz and Reuter, USP 2,300,636.

[18] Hughes and Geigy, BP 579,063.

[12] See p. 575.

[19] Geigy, BP 352,878.

[20] Geigy, BP 495,552.

[21] IG, BP 517,335.

[2] See p. 570.

[22] Geigy, BP 589,536.

POLYKISAZO DYES

A commercial pentakisazo dye is Dianil Fast Brown B (MLB) (salicylic acid ← benzidine $\xrightarrow{\text{alk.}}$ γ-acid → *m*-phenylenediamine ← benzidine → salicylic acid). Columbia Catechin O (AGFA) (salicylic acid $\xleftarrow{2}$ *o*-tolidine $\xrightarrow{3}$ *m*-phenylenediamine $\xleftarrow{1}$ *m*-phenylenediamine-4,6-disulfonic acid $\xrightarrow{1}$ *m*-phenylenediamine $\xleftarrow{3}$ *o*-tolidine $\xrightarrow{2}$ salicylic acid) is a hexakisazo dye. Diamine Catechin 3G (C) (salicylic acid $\xleftarrow{2}$ benzidine $\xrightarrow{3}$ Cleve acids $\xrightarrow{4}$ phenol $\xleftarrow{1}$ 1,5-diaminonaphthalene-3,7-disulfonic acid $\xrightarrow{1}$ phenol $\xleftarrow{4}$ Cleve acids $\xleftarrow{3}$ benzidine $\xrightarrow{2}$ salicylic acid) is an octakisazo dye.[6]

Dyes containing more than four azo groups are useful leather dyes. Hexakisazo dyes, which yield blacks on leather of good fastness and free from rusty tinge, are made according to one of the two schemes: $(\mathrm{A} \xrightarrow{\text{acid}} \mathrm{Z}^1 \xleftarrow{\text{alk.}} \mathrm{D}^1 \longrightarrow \mathrm{Z}^2 \longleftarrow \mathrm{D}^1 \xrightarrow{\text{alk.}} \mathrm{Z}^1 \xleftarrow{\text{acid}} \mathrm{A})$ or $(\mathrm{A} \xrightarrow{\text{2. alk.}} \mathrm{Z}^1 \xleftarrow{\text{1. acid}} \mathrm{D}^2 \longrightarrow \mathrm{Z}^2 \longleftarrow \mathrm{D}^2 \xrightarrow{\text{1. acid}} \mathrm{Z}^1 \xleftarrow{\text{2. alk.}} \mathrm{A})$ in which Z^1 is H-acid, D^1 is a benzidine derivative, Z^2 is *m*-phenylenediamine or resorcinol, and D^2 is *p*-phenylenediamine. Gray to black heptakisazo dyes for leather are claimed by coupling two moles of a diazo-disazo compound (e.g., ← benzidine → H-acid ← A) with a thrice-coupling component such as resorcinol or *m*-phenylenediamine, and then coupling with a diazonium salt.[23]

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[6] See p. 570.

[23] Williams (Hounslow) and Ackroyd, BP 580,122.

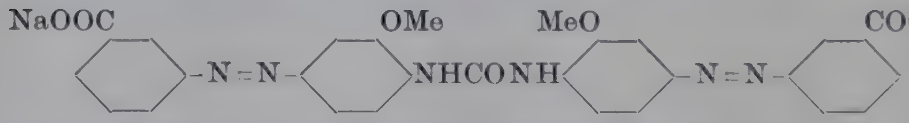
CHAPTER XVI

UREA AND CYANURIC ACID DERIVATIVES

Two important methods for the preparation of disazo, trisazo, and polykisazo dyes are to link two azo dyes, or azo dye intermediates, containing primary amino groups by means of phosgene or cyanuric chloride.[1-6] The second procedure is more recent and has certain advantages over the older phosgenation method, but both are widely used and continue to be the subject of patents.

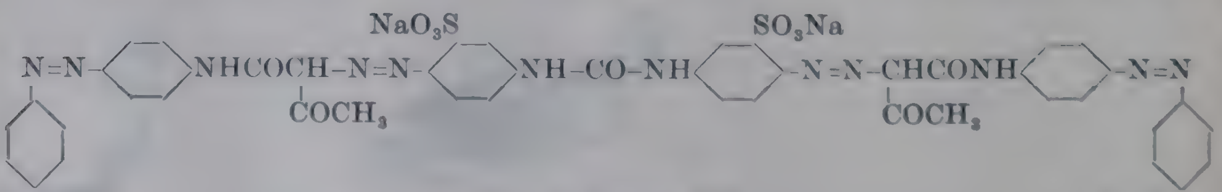
UREA DERIVATIVES

The dyes prepared from carbonyl-J-acid and from tetrazotized 4,4′-diaminodiphenylurea, described in Chapter XII, can also be prepared by condensing two moles of an aminoazo dye (or one mole each of two different aminoazo dyes) with phosgene. This method is usually more convenient, and for some dyes the only one available. An example of a disazo dye derived from urea that can only be prepared by the phosgenation of two moles of a monoazo dye is Benzo Fast Yellow 4GL extra (Günther and Hesse, 1908) (By; CI 349) (Sirius Yellow G, IG)[5] prepared by condensing two moles of the monoazo dye (*m*-aminobenzoic acid → *o*-anisidine) with phosgene. According to Fierz-David[7] several dyes, prepared by phosgenation of two moles of a monoazo dye of the type (2-naphthylamine-4,8-disulfonic acid → *o*-anisidine or *m*-toluidine) or (2-naphthylamine-6,8-disulfonic acid → *o*-anisidine) are offered under the name Benzo Fast Yellow RL. The Benzo Fast Yellows have dyeing and fastness properties similar to those of Chrysophenine, but are cheaper to make.



Benzo Fast Yellow 4GL extra

Dianil Yellow GW (IG), developed recently in the IG laboratories, is an example of a yellow tetrakisazo dye from a phosgenated intermediate.



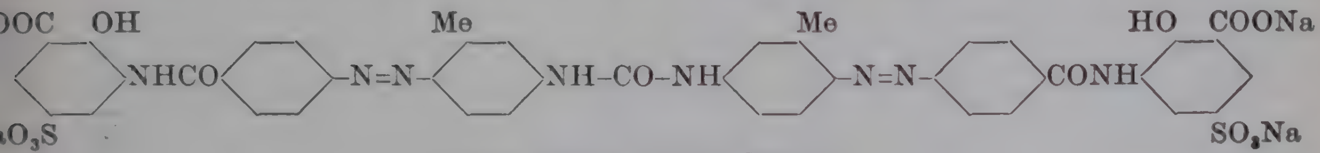
Dianil Yellow GW

[1-6] As in Chapter XII.

[7] Fierz-David, Künstliche Organische Farbstoffe, Springer, Berlin, 1926.

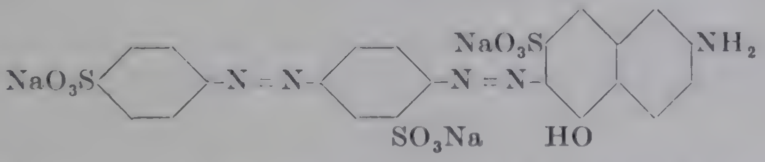
It is prepared from 4,4′-diaminodiphenylurea-3,3′-disulfonic acid, which is tetrazotized and coupled with two moles of 4-acetoacetamidoazobenzene-4′-sulfonic acid. The dye has very good affinity for cellulose fibers and the fastness to washing at 40° is good (3); but the light fastness is low (3).[3]

Several direct cotton dyes of the Sirius and Sirius Supra series (IG) are urea derivatives prepared by the phosgenation of monoazo or disazo dyes containing a primary amino group. Sirius Supra Yellow R extra[2] (2-naphthylamine-4,8-disulfonic acid⟶*m*-toluidine; phosgenate) has very good light fastness (6) and excellent fastness to alkali (5). Sirius Yellow R extra is (C-acid⟶*m*-toluidine; phosgenate).[5] Sirius Yellow 2G has light fastness 5 and washing fastness 2; it is prepared by the phosgenation of the monoazo dye (*p*-nitroaniline⟶salicylic acid; reduce with sodium sulfide).[5] Sirius Supra Yellow FRRL is a new and valuable addition to this range.[3] The clear yellow shades have high light fastness (6–7) and good fastness to washing (3). The pale green shades produced by admixture with blues such as Sirius Supra Blue FFGL have excellent fastness to light. Thiazole Yellow GL (IG) has been stated[6] (contrast CI 813) to be (*p*-aminoacetanilide⟶2-methylindolesulfonic acid; hydrolyze the acetyl group and phosgenate).

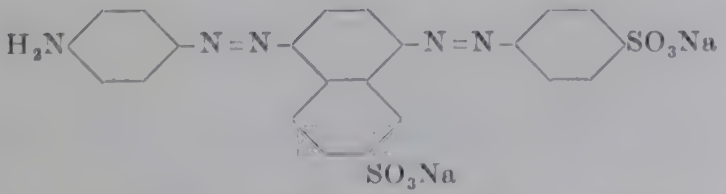


Sirius Supra Yellow FRRL

Sirius Red F3B, prepared by the phosgenation of (I), is a new dye which surpasses all the red dyes of the Sirius and Sirius Supra range in fullness and brilliance.[3] It has excellent leveling properties, good fastness to light (5) and moderate fastness to washing (2–3), which may be improved by treatment with Solidogen BSE (see Chapter XVII). Sirius Supra Brown 3RL is the tetrakisazo dye obtained by the phosgenation of (II). For preparing (II), diazotized benzeneazonaphthylaminedisulfonic acid



(I)



(II)

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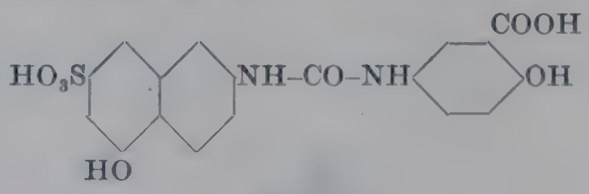
[3] See p. 580.
[2] See p. 580.
[5] See p. 580.
[6] See p. 580.

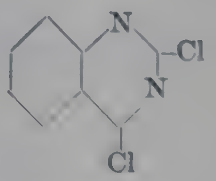
is coupled with *N*-methylaniline-ω-sulfonic acid (aniline + formaldehyde + sodium bisulfite), and the free amine liberated by alkaline hydrolysis.[3] The yellowish brown shades on cotton have good fastness to light. Sirius Supra Brown G is a hexakisazo dye prepared by the phosgenation of the trisazo dye (4-aminoazobenzene-3,4′-disulfonic acid $\longrightarrow$ *m*-toluidine $\longrightarrow$ *m*-toluidine); it has very good light fastness (6) and excellent fastness to alkali (5), but is sensitive to acid.[2] Diazo Brown 3G (IG) is (6-oxalylamido-*o*-toluidine-4-sulfonic acid $\longrightarrow$ cresidine; phosgenate and saponify).[6] Bluish-red dyes with good fastness on vegetable fibers are prepared by phosgenation of the amine obtained by reduction of the dye (*p*-nitroaniline $\xrightarrow{\text{acid}}$ 2R-acid).[7a]

The color of a urea derivative is approximately the sum of the colors of the two azo dyes that have been linked together; but the aqueous alkaline condensation of two azo dyes with phosgene cannot usually be carried out in two stages ($\text{A–NH}_2 \longrightarrow \text{A–NHCOCl} \longrightarrow \text{A–NH–CO–NH–B}$), and the desired compound cannot be obtained as the sole product to the exclusion of the other urea derivatives that can also be formed from the same reactants: A–NH–CO–NH–A and B–NH–CO–NH–B. Nevertheless, unsymmetrical condensations with phosgene are carried out where the shade or other requirements necessitate the linking up of two different intermediates or dyes.[8] An example of the preparation of an intermediate of this type is the phosgenation of J-acid and aminosalicylic acid to form (III), which is useful for the preparation of direct cotton dyes suitable for metallization.

Mixed ureas of azo and anthraquinone dyes for the production of greens have been prepared by condensing the urethane from an aminoazobenzene with 1-amino-4-(*p*-amino)arylaminoanthraquinone-2-sulfonic acid.[9] Phosgenation and cyanuration are frequently mentioned together in patents as alternative methods for linking up azo dye units or intermediates. In addition to phosgenation and cyanuration, methods suggested for linking up two dye molecules or their components are the use of thiophosgene,[10]

(III)





(IV)

dichloroquinazoline (IV), dichloropyrimidine[11] and 3,5-dichloro-1-phenyltriazine.

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[3] See p. 580. [2] See p. 580. [6] See p. 580.

[7a] Bestehorn and Grimmel, BP 622,941. Cf. CI 348.

[8] E.g., Ciba, BP 583,849; 634,130; USP 2,491,566; Geigy, BP 632,944.

[9] IG, SP 232,889. [10] Allied Chemical and Dyestuff, USP 2,384,283.

[11] Ciba, BP 515,066; IG, BP 288,159; 309,102 ; 315,431.

1,3,5-TRIAZINE DERIVATIVES

Fierz-David and Matter[12] have studied the preparation and properties of dyes containing the 1,3,5-triazine ring, which have appeared in the market since 1924 and are the subject of numerous patents.[13] The introduction of the triazine ring by suitable condensations with cyanuric chloride, which may be briefly described as cyanuration, is not merely a convenient procedure for combining azo or other dye units to form more complex dyes. Special properties have been claimed for cyanurated dyes, such as high tinctorial power and purity of the shades, increase in affinity for cellulose fibers, and improvement in fastness. Ciba has included some of the cyanurated azo dyes in its range of Chlorantine Fast colors which are notable for their excellent fastness properties; a few cyanurated anthraquinone vat dyes are among the Cibanone colors. However, the cyanuric ring *per se* does not improve fastness properties.

Cyanuration possesses some advantages over phosgenation. Cyanuric chloride can be condensed with three different amines, giving rise to a very wide variety of products. Condensation with phenols and nuclear condensations analogous to the Friedel-Crafts reaction can also be effected, although these are of little use in the preparation of dyes. Step-wise condensations, leading to unsymmetrical and mixed types of dyes, can be carried out, although it is difficult to obtain homogeneous products. Cyanuric chloride will condense with derivatives of 1,8-aminonaphthols, e.g., H-acid, which cannot be phosgenated.

Preparation of cyanuric chloride (I). The technical importance of cyanurated dyes is indicated by several patents on methods for the preparation of cyanuric chloride. A convenient procedure[14] is to pass gaseous hydrogen cyanide into chloroform containing 1% alcohol, cooled in a freezing mixture, and saturated with chlorine. The presence of alcohol is essential, and it probably functions through the intermediate formation of chloral and its cyanhydrin ($CCl_3\text{–}CHOH\text{–}CN + Cl_2 \longrightarrow Cl_3C\text{–}CHO + CNCl + HCl$).[12] After allowing the reaction mixture to stand for a few days, chloroform is removed and the residue crystallized from ether. A method that gives good quality cyanuric chloride is to pass chlorine into methyl thiocyanate, but the by-products are obnoxious.[15] In the IG process[16] for cyanuric chloride, cyanogen chloride is first prepared by adding chlorine to an aqueous solution of sodium cyanide, sodium chloride and hydrochloric acid. The aqueous solution is distilled, the water is condensed, and cyanogen chloride dried and absorbed in benzene. Dry hydrochloric acid is introduced at 0°, and conversion to cyanuric chloride is effected by agitating the solution for a few hours at 30–40°. Other methods for the second stage of polymerization have been suggested. Gaseous cyanogen chloride may be polymerized at 100–170° in the presence of anhydrous aluminum chloride, and cyanuric chloride removed by vaporization in air or other inert gas.[17] Cyanogen chloride may be polymerized to cyanuric chloride by hydrogen chloride in a mixture of dioxane and chloroform at 0° by allowing to stand for 48 hours. Boron trifluoride may be used to avoid loss of cyanogen chloride with which it forms a nonvolatile derivative.[18] While a melting point of 145–146° has been recorded for cyanuric chloride in the earlier literature, Fierz-David and Matter[12] quote 154°, but give no details for the preparation of pure cyanuric chloride; the higher melting point is obtained by sublimation of the lower melting-point product over anhydrous aluminum chloride.

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[12] *J. Soc. Dyers Colourists* **53,** 424 (1937).

[13] Ciba, DRP 436,179; SP 103,430; 106,074–119; 106,376-410; 109,481; 110,405-07; 110,623–93; 111,274–75; 111,702-13; 131,494; 137,932; 140,415; 143,566-82; 215,147; 236,528; Ciba, BP 209,723; 220,302; 221,843; 242,867; 299,331; 403,222; 588,103; 595,181; IG, BP 300,987; 305,487; 326,791; USP 1,625,530-33; 1,667,312.

[14] Diels, *Ber.* **32,** 692 (1899).

[15] James, *JCS* **51,** 269 (1887).

[16] *BIOS* **661, 1154**.

Cyanuric chloride condensations. The chlorine atoms in cyanuric chloride (I) are as highly reactive as in ordinary acid chlorides, but at 0° no hydrolysis by water occurs in 12 hours.[12] By heating cyanuric chloride with aqueous alkali, the alkali cyanurate is formed. The action of ammonia under carefully controlled conditions leads to the replacement of a chlorine atom by the amino group, further action resulting in 2,4-diamino-6-chlorotriazine and melamine. By treatment with sodium alkoxides, mono-, di- and tri-esters may be prepared, as well as aryl esters in a similar manner. The primary condensation product (II: R =OMe) with sodium methoxide is a useful intermediate in the preparation of cyanurated dyes. Aniline and its nuclear substituted derivatives form primary, secondary (III; R^1 and R^2 =NHPh) and tertiary condensation products, the first type being useful intermediates. More complex amines undergo the third condensation with difficulty. The replacement of the first chlorine atom is carried out in a solvent such as benzene at 0°; using water-soluble amines, such as the sodium salts of arylaminesulfonic acids, the condensation may be effected in aqueous solution. Higher temperatures are necessary for the second and third replacements. In the secondary compound (III), the third chlorine atom can be replaced by a hydroxyl or amino group. Colorless condensation products from cyanuric chloride and arylamine sulfonic acids have been suggested as moth-proofing agents for wool.[19] Friedheim[20] has prepared trypanocidal and spirochetocidal arsenicals and antimonials derived from *s*-triazine by reacting an aminobenzenearsonic acid with

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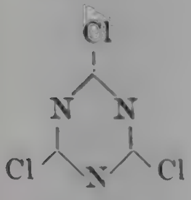
[17] Metcalfe and ICI, BP 566,827.

[18] Oldham and American Cyanamid, USP 2,417,659; Thurston and American Cyanamid, USP 2,416,656.

[12] See p. 583.

[19] Grover and Geigy, BP 543,182.

[20] *JACS* **66**, 1775 (1944); Friedheim, Vogel, and Berman, *ibid.* **69**, 560 (1947); see also Banks *et al.*, *ibid.* **66**, 1771 (1944); **67**, 1947 (1945).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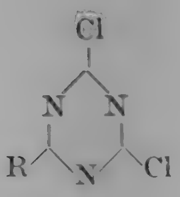
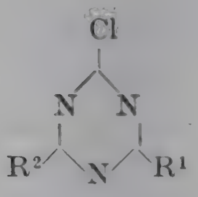

(II)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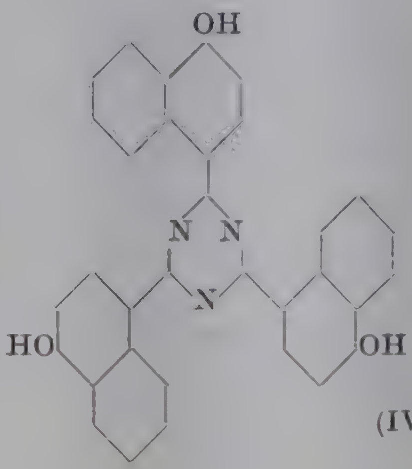
(IV)

cyanuric chloride in alkaline solution, one or two chlorine atoms being later replaced by amino, methylamino, and other groups by treatment of the primary compound with the appropriate base in an autoclave at about 120°. Curd, Landquist, and Rose[21] have prepared a series of primary, secondary, and tertiary condensation products of cyanuric chloride, which they have examined as antimalarials in view of their structural relationship to guanidine and pyrimidine derivatives. Cyanurated derivatives of polymeric ethylenediamine have been claimed as valuable textile assistants for increasing the fastness to washing and perspiration of substantive dyeings.[22]

Cyanurated compounds obtained from intermediates such as H-acid, J-acid, K-acid, aminobenzoic acids and aminosalicylic acid have been described in patents. Fierz-David and Matter[12] have found that by these methods mixtures are usually obtained. Thus, condensing H-acid and J-acid with cyanuric chloride according to the patents, they obtained a mixture of primary and secondary condensation products; but pure primary, secondary or tertiary condensation products can be obtained under specific conditions.

Phenols and naphthols can be condensed with cyanuric chloride in the presence of anhydrous aluminum chloride to give the tertiary condensation products.[23] With α-naphthol Fierz-David and Matter obtained 2,4,6-tris-(4′-hydroxy)-naphthyl-1,3,5-triazine (IV), which is an energetic coupling component of the Naphtol AS type with good affinity for cotton. With simpler diazonium salts, bordeaux shades are produced, and fast black shades with diazotized amino- or diaminoazo compounds.[24] Such cyanurated compounds do not appear, however, to be in the commercial range of "naphthols" (see Chapter XXII).

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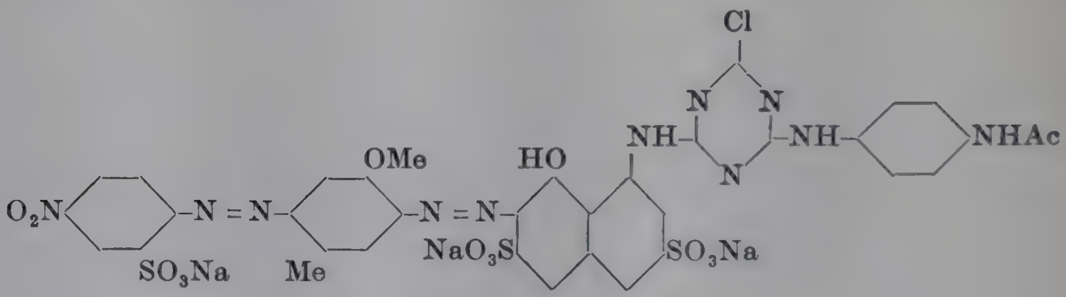
[21] *JCS* 154 (**1947**).

[22] IG, BP 423,864; 423,933.

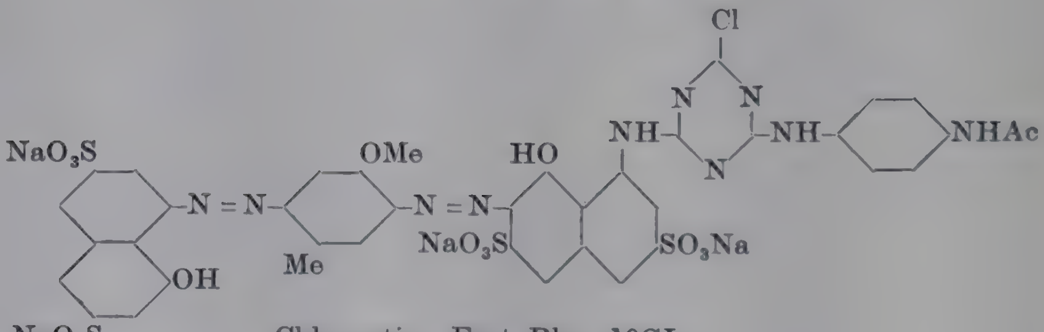
[12] See p. 583.

[23] Ciba, DRP 433,100; USP 1,155,095; SP 107,619; 108,191; 111,500; 119,363; 119,366.

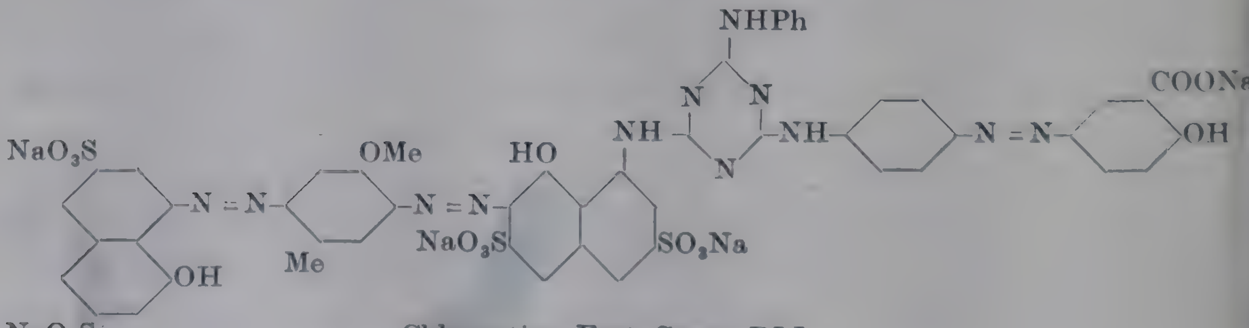
Constitution of some Chlorantine Fast colors. Fierz-David and Matter have identified four direct cotton dyes of the Chlorantine Fast series (Ciba) as cyanurated compounds, and have determined their constitution.[12,25] By the usual methods of reductive fission with alkaline hydrosulfite, cleavage occurred at the azo group without affecting the triazine ring, which was present unaltered in the reduction products; these were isolated and identified by characteristic color reactions. The constitution of each dye was confirmed by synthesis. Chlorantine Fast Rubine RLL (see Chapter XIII) is of interest as a copper complex and a dye in which the triazine residue replaces the carbonyl group in the commonly used urea of J-acid. Chlorantine Fast Green BLL is a good example of the use of cyanuric


Cl
N
N
NH
NH
N
NHAc
OMe
HO
O_2N
N = N
N = N
NaO_3S
SO_3Na
SO_3Na
Me

Chlorantine Fast Blue 8G


Cl
N
N
NH
NH
N
NHAc
NaO_3S
OMe
HO
N = N
N = N
NaO_3S
SO_3Na
OH
Me
NaO_3S

Chlorantine Fast Blue 10GL


NHPh
N
N
NH
NH
N
N = N
COONa
OH
NaO_3S
OMe
HO
N = N
N = N
NaO_3S
SO_3Na
OH
Me
NaO_3S

Chlorantine Fast Green BLL

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[24] Ciba, SP 111,123; 111,497–9.

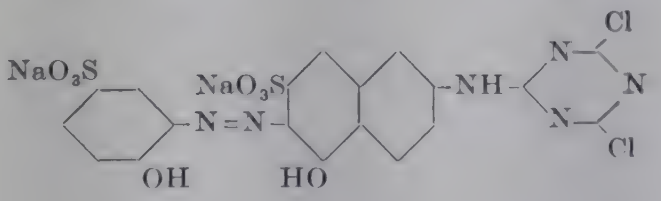
[25] Matter, Dissertation, Zurich, 1936.

[12] See p. 583.

chloride in the production of synthetic dyes of desired shades. A blue and a yellow component can be joined by means of the triazine ring to give a pure green shade.

A typical procedure[13] for the preparation of a dye such as Chlorantine Fast Green BLL is as follows: A solution of one mole of the disazo dye (H-acid$\longrightarrow$cresidine$\xrightarrow{\text{alk.}}$H-acid) in the calculated amount of aqueous sodium carbonate is added gradually to a suspension of cyanuric chloride (one mole) in water at 0–5° with good stirring. Simultaneously 10% sodium carbonate solution is added so as to maintain the pH at about 6. After 4 hours, the suspension of the primary condensation product is treated with a neutral solution of one mole of sodium *p*-aminobenzeneazosalicylate and stirred for 24 hours at 40°, sodium carbonate solution being added to neutralize the liberated hydrochloric acid. The third component, aniline (two moles, the extra mole as an acid-binding agent), is now added and the mixture heated at 90–95° for 2 hours; the solution is finally made alkaline with sodium carbonate and the dye salted out.

Cyanurated dyes in patents.[26] A series of greenish to reddish yellow dyes for aftercoppering on the fiber are made by linking two or three aminoazo compounds by means of cyanuric chloride, not less than two of the components being yellows; one at least must have an acid amide group or a hydroxyacetamide residue, not more than two azo groups, and an *o*-hydroxycarboxylic group. The last requirement is commonly provided by salicylic acid, but 1-hydroxy-2-naphthoic acid can also be utilized.[27] Copper complexes of cyanurated azo dyes containing groups conferring substantivity for cotton figure in many patents; the complexes may be prepared in substance or the dyes applied to the fiber in the presence of a copper salt. Thus anthranilic acid or an *o*-aminophenol may be diazotized and coupled



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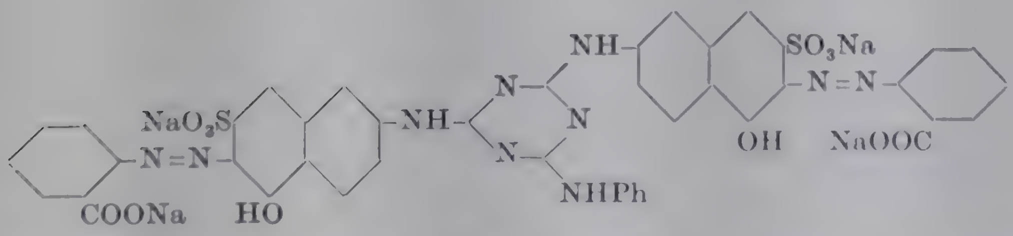

(VI)

with the condensation product of J-acid (one or two moles) with cyanuric chloride or a primary derivative of cyanuric chloride. Two typical dyes which yield substantive copper complexes are (V) and (VI).[28] The copper complex of the azo dye obtained by coupling diazotized 3-amino-4-hydroxybenzanilide with the tertiary condensation product from cyanuric chloride, two molecules of J-acid and one of aniline dyes cotton a fast red shade.[28a]

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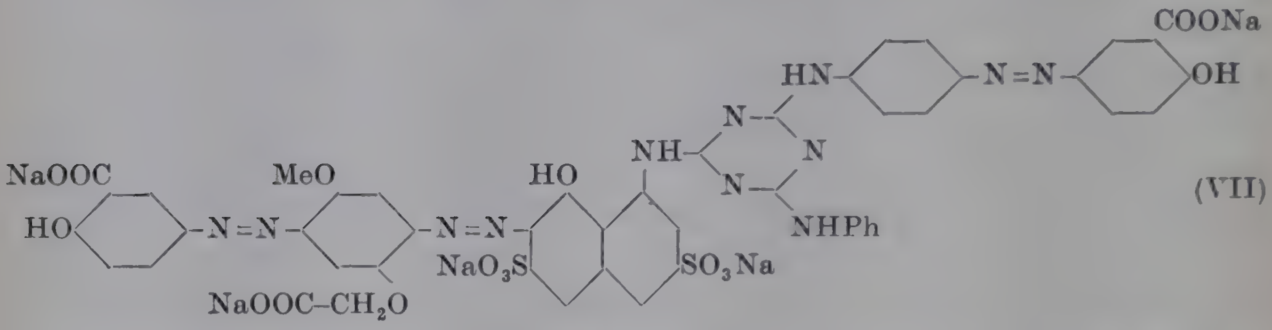
[13] See p. 583.

[26] For a review, see Boyle, *Ind. Chemist* 15, 331 (1939).

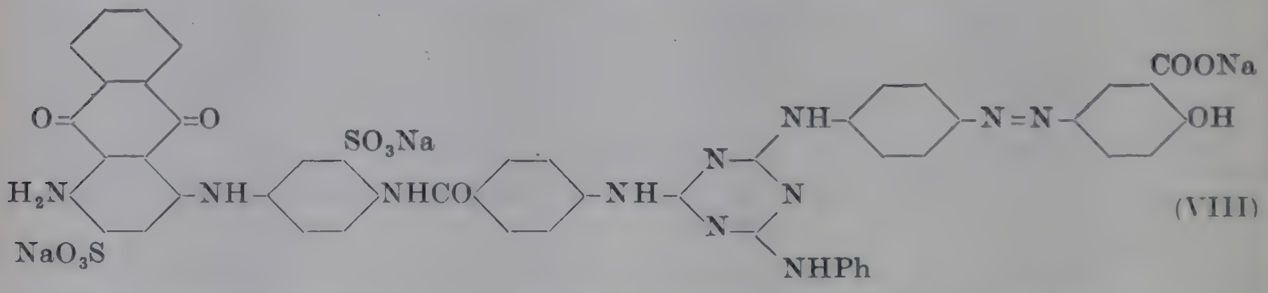
[27] Ciba, BP 546,710.

In the green trisazo dye (VII), the presence of two salicylic acid residues enables the fastness to be increased by aftertreatment with copper.[29] The methoxyl group can be replaced by other alkoxyl groups in which the carbon chain is not more than seven. The trisazo dye (*p*-nitroaniline⟶Cleve acid⟶Cleve acid⟶secondary condensation product of J-acid and metanilic acid with cyanuric chloride) dyes a gray fast to light and boiling.[29a]



(VII)

Mixed azo anthraquinone dyes for cotton are prepared by linking a blue anthraquinone acid color with a yellow azo dye, the resulting green dyes being rendered fast to light by aftercoppering.[30] An example is (VIII); and many variations are possible, a yellower shade of green for instance being obtained by using a second mole of the yellow azo dye instead of aniline.



(VIII)

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[28] Crossley, *Am. Dyestuff Reptr.* **27,** 127 (1938). See also Geigy, SP 228,371–4; Ciba, SP 217,958–67; 228,936; 232,296; 239,342–5; 240,225; USP 2,460,618.

[28a] Ciba, BP 606,872; USP 2,467,621.

[29] Ciba, BP 541,968. See also SP 221,205–6.

[29a] Ciba, BP 608,897.

[30] Ciba, BP 554,463; SP 217,241; USP 2,167,804.

CHAPTER XVII

DIRECT COTTON DYES AFTERTREATED ON THE FIBER

The usual reasons for employing direct cotton dyes such as Congo Red are the low cost and the simplicity of the dyeing process. More recently, direct cotton dyes with improved fastness properties, particularly to light, have been discovered, and it has also been found that some of the older and cheaper dyes can be aftertreated on the fiber, e.g., with copper salts, to improve the light fastness. The nature of the direct dyeing process limits the fastness to washing, but by certain treatments of the dyed fiber it is possible to effect considerable improvement in the fastness to washing. The aftertreatments recommended are: (*a*) diazotization and development; (*b*) development with diazonium salts; (*c*) treatment with formaldehyde; (*d*) treatment with cation-active organic compounds; (*e*) treatment with copper salts; (*f*) treatment with chromium fluoride or sulfate and sodium dichromate.[1-6] The main object of treatment (*a*) or (*b*), by which one or more azo groups are introduced, may be to modify the shade. Although the improvement in fastness is occasionally an empirical observation, the aftertreatment processes are related to the chemical constitution of the dye, and it is of interest to make a brief survey of this relationship.

The practical utility of these methods of aftertreatment is limited by the fact that the advantage of direct dyes is their ready applicability by a single-stage process, and this will be removed by employing additional processes, unless the expenditure of time, labor and material is more than compensated by the modification in the shade or the improvement in the fastness properties. Apparently such possibilities have not been exhausted, since recent patent literature includes numerous examples of direct cotton dyes which are recommended for aftertreatment on the fiber.

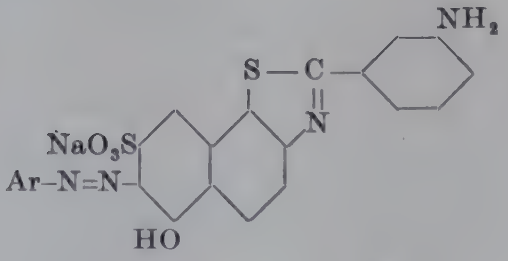
In addition to aftertreatments which involve chemical reaction with the dyes, there are processes using resins in which the primary effect is waterproofing or water repellancy, which then leads to improved fastness of the dyed material to wet treatments. All the usual types of synthetic resins (phenol-, urea-, and melamine-formaldehyde condensates, polyvinyl derivatives) have been suggested; and, as in crease-resistance processes, the resins may be applied in various stages of condensation or polymerization.

[1-6] As in Chapter XII.

DIAZOTIZATION AND DEVELOPMENT

Dyes containing primary amino groups in suitable positions can be diazotized on the fiber, and developed with coupling components, such as resorcinol (Developer F, By), β-naphthol (Developer A, By), *m*-phenylenediamine (Developer E, By), and 1-phenyl-3-methyl-5-pyrazolone (Developer Z, By). Diazotized dyeings must be developed as soon as possible after diazotization in view of the instability of diazonium salts. Among the various methods of aftertreating fibers dyed with azo dyes, this process would *prima facie* appear to be least likely to commend itself to the practical dyer. Diazotization and coupling are processes requiring careful control, and uniform shades are not easy to obtain when these reactions have to be carried out on the fiber. Nevertheless, the large number of commercial dyes of this type[7] and recent patents indicate that the process of diazotization and development is a valuable method of aftertreating direct dyes on the fiber, since washing fastness, lack of which is the main disadvantage of the direct dyes, may thus be appreciably improved. Dyes of this type are also applicable to wool and to union fabrics of cellulose and protein fibers.

Primuline (see Chapter XIX) was the first dye to which the diazotizing and developing (or ingrain color) process was applied (Green, 1887); the fugitive yellow produced by direct dyeing can be converted on the fiber into a range of much faster shades, such as orange with resorcinol and red with β-naphthol. Another thiazole dye to which this method of aftertreatment can be applied is Diazo Brilliant Scarlet BA (I) (By; ST 47);[8] the developer is β-naphthol.



$ArNH_2$ = 55% *o*-toluidine + 45% *p*-toluidine-3-sulfonic acid

(I)

p-Aminoazobenzene and aminoazonaphthalene derivatives in which the amino and azo groups are in the 1,4-positions represent another type of dyes suitable for the diazotization and development process. They may be prepared by (*a*) using aniline or α-naphthylamine or one of their derivatives with the *p*-position free for coupling as end component; or (*b*) using *p*-nitroaniline as a diazonium component and reducing the nitro group to amino; or (*c*) using an *N*-acyl-*p*-phenylenediamine as a diazonium component and hydrolyzing the acyl group. As end component (alkali-coupled) J-acid, an aminobenzoyl-J-acid, γ-acid or H-acid can be used. A combination of these methods is used if two diazotizable amino groups are desired. Naphthogen Blue RR (AGFA)[9] is typical of a dye prepared by method (*a*). Like other trisazo dyes of this type it has high light fastness, and the washing fastness is considerably improved by diazotizing and developing on the fiber with β-naphthol. Diazo Blue 3R (By) is stated to be (mixture of R- and G-acid ⟵dianisidine⟶*m*-toluidine)[6] and Diazo Sky Blue 3G (By) to be (acetyl-K-acid⟵dianisidine⟶*m*-aminoacetanilide).[5] If a disazo dye (A⟶M¹⟶M²), in which A, M¹ and M² are benzene or naphthalene residues linked in the *p*-position and A contains a solubilizing group, is applied to cotton as a direct dye, then diazotized and developed on the fiber with an aroyl-H-acid, the blue or gray shades change to green.[10] Blue to violet trisazo dyes such as (H-acid⟶α-naphthylamine⟶Cleve-6-acid⟶*p*-xylidine), by diazotizing on the fiber and coupling, give shades with improved fastness to washing.

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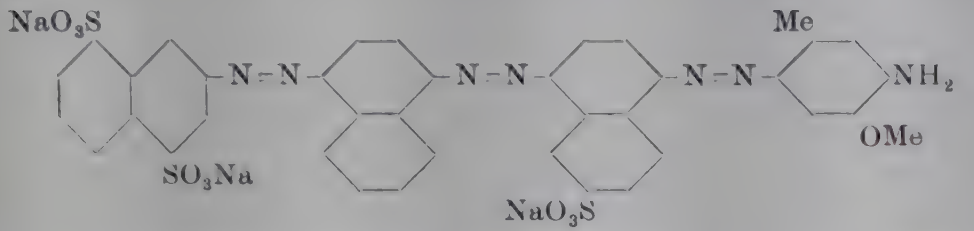
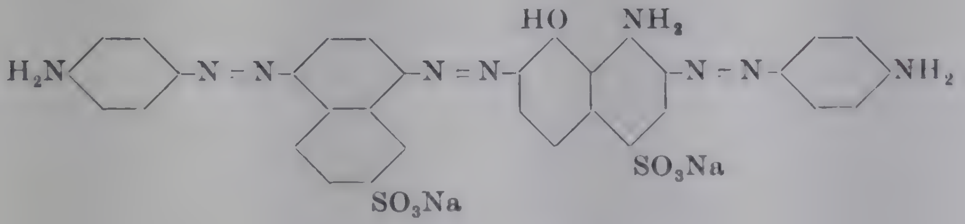
[7] Diaz- or diazo usually occurs in the trade names.

[8] *BIOS* 1157.



Naphthogen Blue RR

Examples of method (*b*) are Zambesi Black D[11] and V, of which the latter is more important technically. Zambesi Black V (AGFA, 1902) is prepared by reducing the nitro group in the monoazo dye (*p*-nitroaniline⟶Cleve acid), semi-diazotizing the diamine, alkali-coupling with the monoazo dye (p-nitroaniline$\xrightarrow{\text{acid}}$S-acid), and reducing nitro to amino. Tetrazotized on the fiber and developed with β-naphthol, it gives a black with good fastness to light and excellent fastness to washing, commonly used for sewing thread. Dyes of the pattern (A⟶M¹⟶M²⟶E), coupled with two moles of β-naphthol, give blue pentakisazo dyes on cotton; A is nitroaryl-



Zambesi Black V

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[9] Fierz-David, Künstliche Organische Farbstoffe, Springer, Berlin, 1926.

[6] See p. 589.

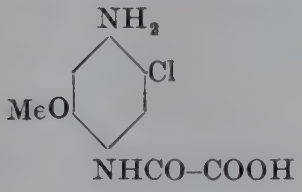
[5] See p. 589.

[10] Geigy, BP 511,103.

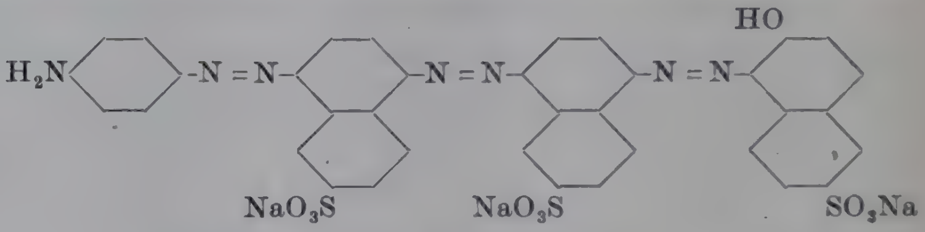
[11] See Chapter XII.

amine, the nitro group of which is eventually reduced to amino; M^1 and M^2 are Cleve acids; and E is an arylamine of the benzene or naphthalene series.[12]

Diaminogen Blue BB (C; CI 316) (4-acetamido-Cleve acid→α-naphthylamine→Schaeffer acid: hydrolyze the acetyl group) dyes direct a valueless greenish-blue, which is converted into a relatively fast dark blue by diazotizing and developing with β-naphthol and into a black with *m*-phenylenediamine. Diaminogen Sky Blue N (C) is (5-acetamido-4-methoxy-*o*-toluidine→Cleve-6-acid→NW-acid; hydrolyze the acetyl group). Diazo Fast Green BL (By; CI 532) (Diazo Fast Green 3GL, IG)[6] (4-acetamido-Cleve-7-acid →Cleve-6-acid $\xrightarrow{\text{alk.}}$ γ-acid →2-methylindole; hydrolyze the acetyl group) is rendered bluer and faster to light and washing by diazotization and development with β-naphthol. Diazo Sky Blue 3GL (II→Cleve-6-acid→1-naphthol-3-sulfonic acid; saponify),[5] Diazo Indigo Blue 4GL extra (II→Cleve-6-acid→Cleve-6-acid→1-naphthol-3-sulfonic acid; saponify), and Diazo Indigo Blue M (*N*-oxalyl-*p*-phenylenediamine →Cleve-6-acid→Cleve-6-acid→Schaeffer acid) are other dyes in this series;[6] diazotized and developed on the fiber with β-naphthol the shades have good washing fastness (3) and light fastness 4, 5–6 and 5–6 respectively. Naphthogen Blue B (AGFA) has been stated to be (*p*-aminoacetanilide→1-naphthol-5-sulfonic acid; saponify;→Cleve-6-acid→cresidine).[6] In Diazo Olive G (By; CI 595) (salicylic acid←benzidine$\xrightarrow{\text{acid}}$S-acid$\xleftarrow{\text{alk.}}$*p*-aminoacetanilide; saponify) the salicylic acid group gives the olive-green shade (diazotized and developed with β-naphthol), good dischargeability in calico printing, but the light fastness is only 2–3.



(II)



Diazo Indigo Blue M

Dyes prepared by alkaline coupling of J-acid, γ-acid or H-acid with a diazonium salt contain a readily diazotizable amino group.

Oxamine Violet (B; CI 393) (benzidine$\overset{\text{alk.}}{\rightrightarrows}$2 moles J-acid) is converted into a navy blue by diazotization and development with β-naphthol, and into a brown with *m*-phenylenediamine; and Oxamine Blue R (B; ST 473) (J-acid$\xleftarrow{\text{alk.}}$*o*-tolidine→NW-acid) dyes a violet-blue, converted into a faster bluish-violet by diazotization and development with β-naphthol. Diamine Heliotrope B (C) is stated to be (acid GR←benzidine$\xrightarrow{\text{alk.}}$J-acid).[6]

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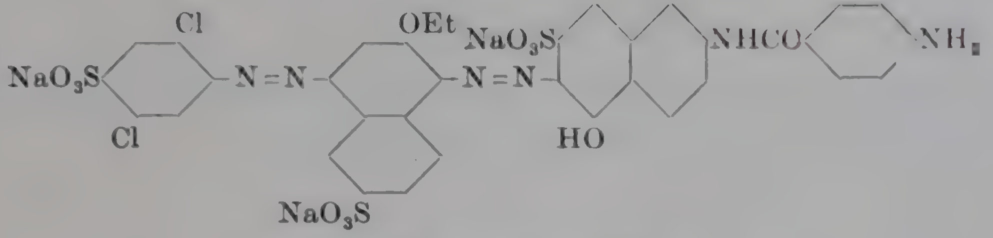
[12] Murphy, Rossander and du Pont, USP 2,153,200–1; see also Froning and du Pont, BP 581,305.

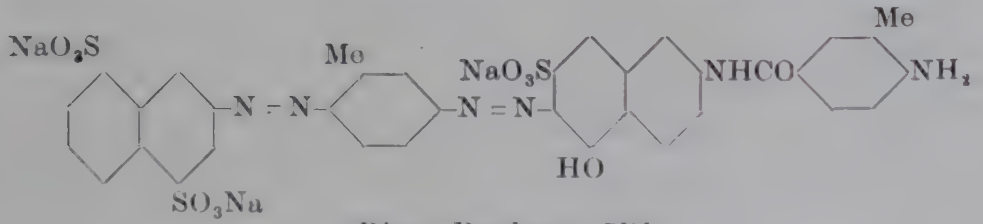
[6] See p. 589.

[5] See p. 589.

Azo dyes having *m*- or *p*-aminobenzoyl-J-acid or *m*- or *p*-aminobenzoyl derivatives thereof as end component constitute an important group of diazotizable dyes. Rosanthrene O and Diazo Brilliant Orange GR extra are early examples of this type.[13] Diazo Brilliant Green 3G (IG) dyes blue-green directly, but on diazotization and development with phenylmethylpyrazolone, a purer, brighter and faster green is obtained.[5, 14] Diazo Bordeaux 7BL (IG) is a new dye for diazotization and development with β-naphthol.[3] The shades have good dischargeability, light fastness 4–5 and washing fastness 4–5 at 40°. The disazo dyes (A→M→*m*-amino-*p*-methoxybenzoyl-J-acid), diazotized and developed on the fiber with β-naphthol, give "excellent bright shades."[15] The shades from the disazo dyes (5-*p*-aminobenzamido-salicylic acid→M→*p*-aminobenzoyl-J-acid), diazotized and developed on the fiber with β-naphthol, show unexpected improvement in light fastness when treated with anticrease agents.[16] The dye (III) dyes cotton a bluish green, converted into a deep green by tetrazotization on the fiber and development with phenylmethylpyrazolone.[17] Blue to gray trisazo dyes such as (metanilic acid→Cleve-7-acid→2,5-dimethoxyaniline→2-*p*-aminobenzamido-6-naphthol-8-sulfonic acid)



Diazo Brilliant Green 3G



Diazo Bordeaux 7BL

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[6] See p. 589.

[13] Diamine Fast Red 5B is (4-aminoazobenzene-4′-sulfonic acid→*p*-aminobenzoyl-J-acid); Ref. 9.

[5] See p. 589.

[14] An apparently erroneous structure is given for this dye in ST 598, quoting Ref. 9, p. 157. According to *FIAT* **764,** Diazo Brilliant Green 6G (IG) is (3-chloro-*o*-toluidine-5-sulfonic acid→2-ethoxy-Cleve-6-acid→*p*-aminobenzoyl-H-acid).

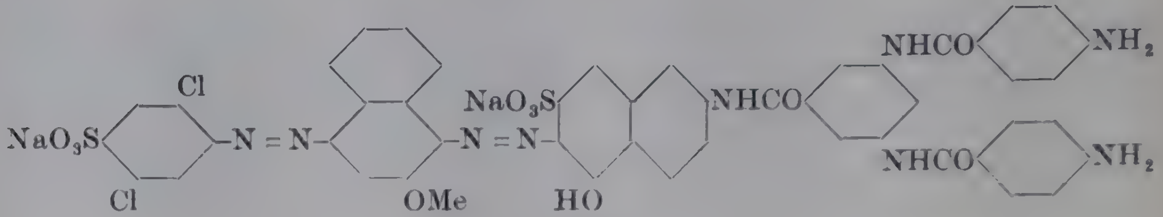
[3] See p. 589.

[15] Sparks, Trepagnier and du Pont, BP 586,663.

[16] Grandjean and Sandoz, USP 2,458,776.

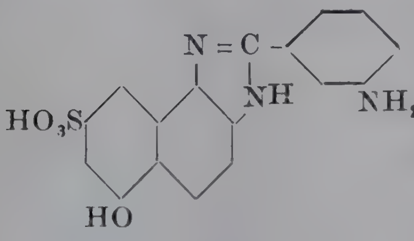
[17] Ciba, BP 513,109.

develop on the fiber to green by diazotizing and coupling with 1-phenyl-3-methyl-5-pyrazolone.[10]

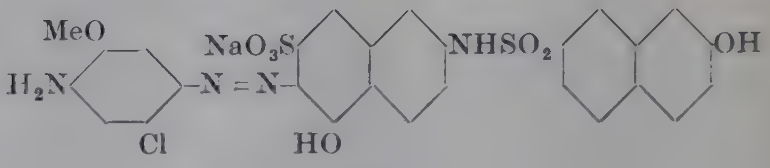


(III)

Diamine Azo Scarlet 4BL extra (C; CI 322) (Sulfanilic acid$\longrightarrow$IV$\longrightarrow$IV) is of interest as a heterocyclic derivative of J-acid.



(IV)



(V)

Diamine Black RO (C; CI 395) (benzidine$\xRightarrow{\text{alk.}}$γ-acid, 2 moles) dyes a grayish violet, changed to black by diazotization and development with *m*-phenylenediamine, and to blue-black with β-naphthol. Benzo Sky Blue (Dianisidine$\xRightarrow{\text{alk.}}$2 moles H-acid) is for development with phenylmethylpyrazolone. Diamine Black BH (C; CI 401) (H-acid$\xleftarrow{\text{alk.}}$benzidine$\xrightarrow{\text{alk.}}$γ-acid) dyes cotton direct blue, converted into a black by diazotization and development with *m*-phenylenediamine.

A self-coupling treatment can be applied to dyes (or substantive intermediates) which contain both a diazotizable amino group and a coupling position. When such a compound is treated with nitrous acid, the probable mechanism of the reaction is that one molecule of the diazonium salt couples in the available position in a second molecule, and the process is perhaps repeated to form polykisazo dyes. An example is *m*- or *p*-aminobenzamido-J-acid, which has affinity for cotton and (like Diazo Light Yellow 2G) may be considered to be a colorless dye. The monoazo dye (V) dyes violet on wool or staple fiber; by treatment with nitrous acid on the fiber diazotization and self-coupling take place, the shade changing to blue.[18] The second coupling will take place in the 1-position in the β-naphthol residue, and the fastness of the developed dye may be improved by treatment with copper or chromium salts (see also Autazol Chrome Black BA).[11]

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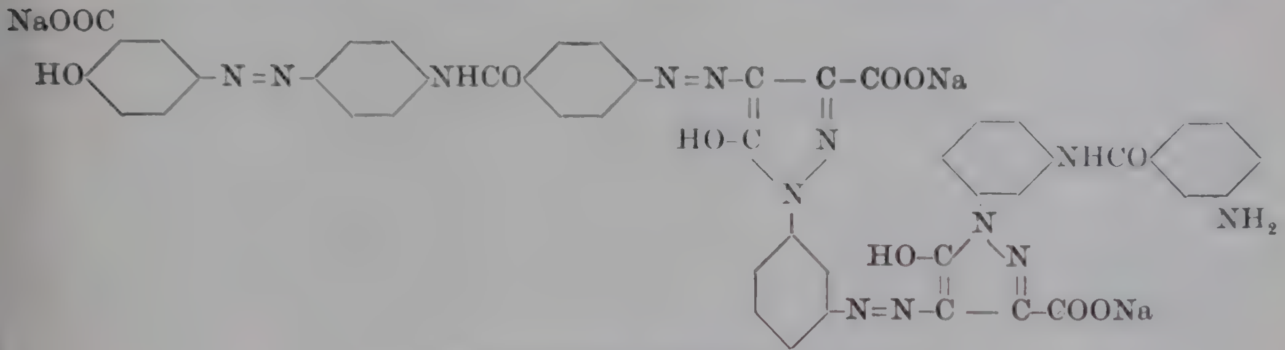
[10] See p. 591.

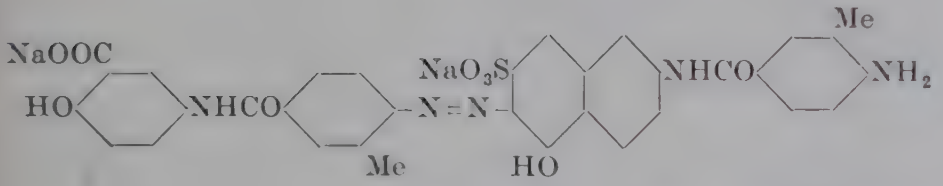
[11] See p. 591.

[18] Kracker and Schumacher, USP 2,205,481.

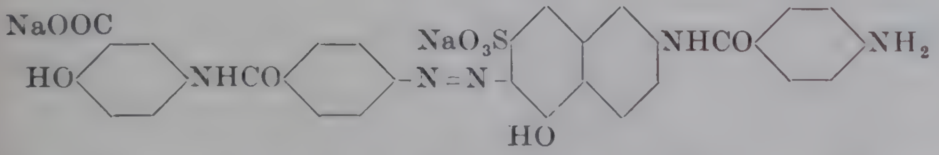
Developed dyes for discharge printing. For obtaining good dischargeability azo dyes containing a salicylic acid residue are especially suitable. Diazo Golden Yellow G extra (IG) is a new dye which develops on the fiber with β-naphthol or phenylmethylpyrazolone to a golden yellow (the latter developer leading to a purer shade); the shades can be satisfactorily discharged under both neutral and alkaline conditions. Diazo Brilliant Scarlet 3BL extra and Diazo Fast Scarlet FBL are other examples, the recommended developing agent being β-naphthol.[3]



Diazo Golden Yellow G extra



Diazo Brilliant Scarlet 3BL extra



Diazo Fast Scarlet FBL

COUPLING WITH DIAZONIUM SALTS

Azo dyes which couple on the fiber with diazonium salts usually contain resorcinol or *m*-phenylenediamine or *m*-aminophenol as an end component; and since this is also true of azo dyes capable of aftertreatment with formaldehyde, such dyes may be submitted to either treatment depending on shade and fastness requirements. The introduction of an additional azo group will have a bathochromic effect on the shade, and the fastness properties, especially to washing, are often simultaneously improved. For two reasons, one of which is its cheapness, the only diazonium salt used in practice is from *p*-nitroaniline. The other reason is that coupling on the fiber has to be carried out in a relatively short time in comparison with the preparation of an azo dye in substance; the diazonium salt must therefore be a rapid coupler. "Developing" in this section refers therefore to the coupling of a dye on the fiber with diazotized *p*-nitroaniline.

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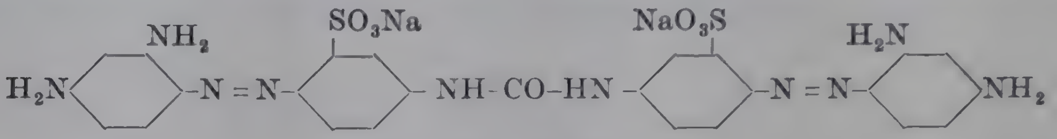
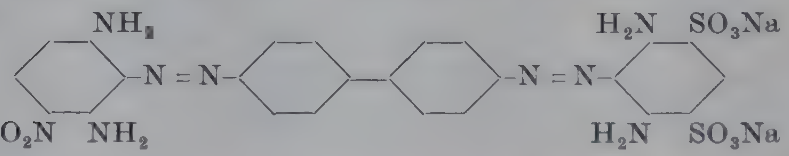
[3] See p. 589.

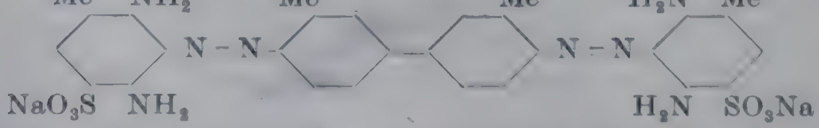
A simple dye suitable for the developing process is Benzo Brown D3G extra (By; CI 273) (sulfanilic acid → aniline → *m*-phenylenediamine). Para Fast Brown GR (By; CI 352) develops to a bright brown with good fastness to washing (3–4). Para Brown V extra (IG) (*m*-phenylenediamine ← benzidine $\xrightarrow{\text{alk.}}$ 2R-acid → *m*-phenylenediamine)[6] and Para Brown RK (IG) are also typical of dyes for the development process which contain *m*-phenylenediamine residues. Para Brown RK is prepared by coupling diazotized *N*-monoformyl-*m*-phenylenediamine with γ-acid, hydrolyzing the formyl group, tetrazotizing this diamine, and coupling with 2 moles of a mixture of 20% *m*-phenylenediamine-4-sulfonic acid and 80% *m*-aminophenylglycine.[2] Diamine Brown V (γ-acid $\xleftarrow{\text{alk.}}$ benzidine → *m*-phenylenediamine)[11] is suitable both for diazotization-development and for coupling with diazotized *p*-nitroaniline; improved fastness to washing, together with deepening of the shade, is obtained both ways. A dye in which the first coupling of a *m*-phenylenediamine derivative takes place in the 2-position and the second coupling on the fiber in the 6-position is Pyramine Orange 3G (B; CI 368). The molar proportions of diazonium salt which react and the sites of coupling are often obscure. Primuline may be developed, coupling presumably taking place *ortho* to the amino group. Diamine Bronze G (C; CI 559) (salicylic acid ← benzidine $\xrightarrow{\text{alk.}}$ H-acid → *m*-phenylenediamine) dyes cotton direct a yellowish-brown, changed by development to an olive. In Toluylene Orange R (GrE; CI 446) and G, which dye cotton orange converted by development into a full reddish-brown with improved fastness to washing, there is no unsubstituted coupling position; the sulfonic groups may be displaced, but the products of coupling have not been examined. Two largely used dyes for which various methods of aftertreatment (development; diazotization-coupling; formaldehyde;



Para Fast Brown GR



Pyramine Orange 3G



Toluylene Orange R

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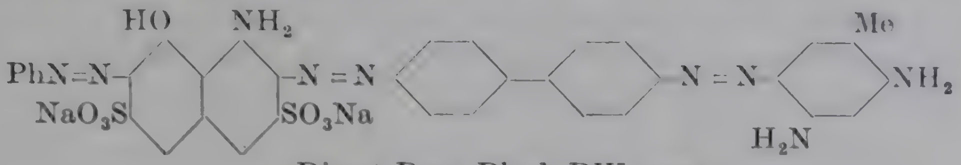
[6] See p. 589.

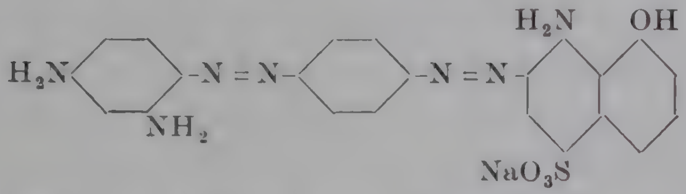
[2] See p. 589.

[11] See p. 591

copper sulfate and dichromate) are recommended are Direct Deep Black EW and RW extra (Müller, 1901) (By; CI 581 and 582). The alteration


Direct Deep Black RW extra

in shade of Para Black R (Kahn, 1909) (By; CI 339) by development from a blue to a black indicates the entry of more than one azo

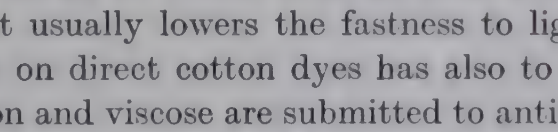

Para Black R

group. The IG Manual includes Chicago Blue B (By; CI 516) (S-acid $\xleftarrow{\text{alk.}}$dianisidine$\xrightarrow{\text{alk.}}$S-acid) in the developing class, but from the CI constitution this is inexplicable.

The tetrakisazo dye (resorcinol$\longleftarrow$*p*-phenylenediamine$\xrightarrow{\text{alk.}}$$\gamma$-acid$\longrightarrow$ α-naphthylamine$\longrightarrow$resorcinol) yields fast black shades on cotton by development.[19] The wash-fast olive-black shades obtained by developing the dye (*m*-aminophenol$\longleftarrow$M-acid$\longleftarrow$*p*-phenylenediamine$\longrightarrow$*m*-aminophenol) on the fiber with *p*-nitroaniline are dischargeable to a pure white.[19a]

Treatment with Formaldehyde

The aftertreatment of certain direct dyes on the fiber with formaldehyde (1–2% of 40% formalin on the weight of the material) in presence of acetic or formic acid (about 0.3%) at 60° for half an hour increases the fastness to wet treatments, but usually lowers the fastness to light. This adverse effect of formaldehyde on direct cotton dyes has also to be borne in mind when direct-dyed cotton and viscose are submitted to anticreasing and other finishing treatments involving the use of formaldehyde. The dyes to which the formaldehyde process is applicable are mainly derived from *m*-phenylenediamine, resorcinol, and *m*-aminophenol as end components. The chemistry of the reaction is obscure. Aromatic amines and phenols react with formaldehyde in several ways, depending on the conditions of the reaction,



to form benzyl alcohol derivatives, diphenylmethanes, or high polymers. Fierz-David[9] has suggested that diphenylmethane derivatives of the indicated type are formed, the increase in molecular weight leading to the improved washing fastness. The diphenylmethane skeleton may be responsible for the decrease in light fastness in view of the poor light fastness of other groups of diphenylmethane and triphenylmethane dyes. Fourness[20] has shown that the aftertreated dyes still contain primary amino groups; when Direct Deep Black EW and RW are dyed in pale shades, diazotized on the fiber and coupled with β-naphthol, similar color changes take place whether the dyeing has been aftertreated with formaldehyde or not. According to Walker,[21] formaldehyde links the dye molecule with the cellulose molecule; although the interaction of formaldehyde with cellulose usually requires much higher temperatures and the presence of mineral acid catalysts, this suggestion must be considered in the light of such facts as the slow combination of cellulose with formaldehyde to form a methylene ether to about 0.3% in the presence of lactic acid at 40–50°, and the curious effect of formaldehyde in promoting the solubility of cellulose in aqueous calcium thiocyanate in the cold, while a temperature of 80–100° is required in the absence of formaldehyde.

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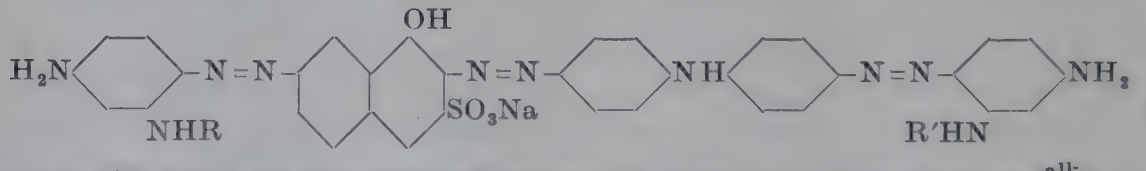
[19] Ciba, BP 564,024. See also Ciba, BP 573,025.

[19a] Ciba, SP 227,494–6.

[9] See p. 591.

Some of the commercial dyes for formaldehyde treatment include "form" in the group names; e.g., Plutoform (By), Benzoform (By), Azoform (S), Formal (Gy), Erieform (NAC), Calcoform (AC), Formanil (AAP), Pharmaform (PhC), Polyform (du Pont). The Vulcan colors (Lev; BDC) were among the early representatives of this class.

Plutoform Black BL, L, 3GL (CI 545) (VI; R and R′ $=CH_2COONa$), Plutoform Black G (VI; $R=H$; $R'=CH_2COONa$),[11] Pluto Black 5BS extra (CI 544) (*m*-phenylenediamine $\leftarrow$ diaminodiphenylamine $\xrightarrow{\text{alk.}}$ γ-acid $\xrightarrow{\text{alk.}}$ γ-acid), and Columbia Black FF extra[11] are useful black trisazo dyes for formaldehyde treatment, in which one or both the end components is *m*-phenylenediamine or a derivative. These aftertreated blacks have good fastness to washing and to cross dyeing with acid dyes, and they are useful for dyeing sewing thread, dyeing cotton-wool unions, and calico printing. Benzoform Brown FC is (salicylic acid $\leftarrow$ *N*-*p*-aminobenzoyl-*p*-phenylenediamine $\xrightarrow{\text{alk.}}$ γ-acid $\rightarrow$ *m*-phenylenediamine).[6]



(VI)

Examples of dyes for formaldehyde treatment in which resorcinol is an end component are: Benzoform Orange G (a derivative of 4,4′-diaminodiphenylurea-3,3′-disulfonic acid $\rightrightarrows$ two moles resorcinol); Benzoform

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[20] *J. Soc. Dyers Colourists* **63**, 179 (1947); Contrast Whittaker, *ibid.* 38.

[21] Formaldehyde, Reinhold, New York, 1944, p. 366.

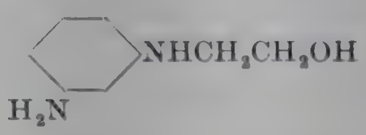
[11] See p. 591.

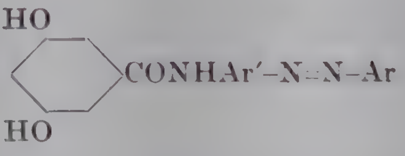
[6] See p. 589.

Blue BBL (*p*-aminoacetanilide→Cleve-7-acid→Cleve-7-acid→resorcinol; hydrolyze the acetyl group) which is stated[6] to have good fastness to light, but is graded only 2 in the IG Manual; Benzoform Green FFG and FFL (4-oxalamidoaniline-2-sulfonic acid→2-ethoxy-1-naphthylamine→*m*-aminobenzoyl-J-acid or IV→resorcinol; saponify);[22] and Benzoform Brown R (γ-acid$\xleftarrow{\text{alk.}}$diaminodiphenylurea→resorcinol).[6]

Disazo and polyazo dyes for aftertreatment with formaldehyde, in which resorcinol or *m*-aminophenol is the end component, continue to be the subject of patents, the schemes of preparation being variations of known procedures, employing the usual types of symmetrical diamines or other components known to yield substantive dyes.[23] One example is the red dye (sulfanilic acid→aniline→*p*-aminobenzoyl-J-acid→resorcinol). In the Formal Fast Black (Plutoform Black) type of dye in which *m*-phenylenediamine or one of its derivatives is the end component,

(VII)





(VIII)

the use of *N*-hydroxyalkyl-*m*-phenylenediamine (e.g., VII) leads to brighter shades and better dischargeability.[24] Tetrakisazo dyes for formaldehyde treatment are obtained by such schemes as (*m*-aminophenol←diamine $\xrightarrow{\text{alk.}}$J-acid→$\alpha$-naphthylamine→resorcinol or *m*-aminophenol).[19] Tetrakisazo dyes (E←M←D→M→E) in which E is resorcinol or a 5-substituted resorcinol give bright shades on cotton which are improved in washing fastness without loss of brightness by aftertreatment with formaldehyde.[25, 26] Increase in both light and washing fastness after formaldehyde treatment is claimed for the dyes (naphthol- or *N*-substituted naphthylaminesulfonic acid←a benzidine→an α-naphthylamine→resorcinol).[27] Direct dyes of the form (VIII) containing a terminal 3,5-dihydroxybenzamido group are suitable for formaldehyde treatment, and yield dyeings of greater brightness and light fastness than similar dyes containing an azoresorcinol terminal group.[28] In (VIII) Ar′ contains additional azo groups.

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[6] See p. 589.

[22] IG, BP 519,644.

[23] du Pont, USP 2,228,415–6; 2,249,045; 2,249,334; 2,234,201; 2,263,894; 2,322,740; 2,322,750; Geigy, BP 634,429.

[24] IG, BP 470,407.

[19] See p. 597.

[25] Sparks and du Pont, USP 2,234,201.

[26] See also du Pont, USP 2,204,229–30; 2,448,158.

[27] du Pont, USP 2,370,500.

[28] du Pont, USP 2,416,547; 2,195,089.

CATION-ACTIVE ORGANIC COMPOUNDS

A recent method of aftertreatment of direct cotton dyeings is to treat the dyed material with organic ammonium salts possessing surface activity and forming insoluble complexes with the dyes. The reaction consists essentially in a combination of the cation of the cation-active reagent with the dye anion, in the same way as the formation of arylammonium salts of aromatic sulfonic acids by the interaction of the amine hydrochloride with the sodium sulfonate: $(ArSO_3Na + \overset{-}{Cl}\overset{+}{N}R_4 \rightarrow Ar\overset{-}{SO_3}\,\overset{+}{N}R_4 + NaCl)$. Since the direct cotton dyes in general are aromatic sodium sulfonates, the reaction is applicable in principle to all direct dyes, but in practice the process is recommended for a strictly limited range of dyes in conjunction with each commercial product of this type. The object of the aftertreatment is to obtain improved fastness to water, washing, cross-dyeing with acid colors and damp ironing, and the degree of improvement actually attained will depend on the stability of the dye-reagent complex. These ammonium salts are comparatively stable to water and acids, but they are readily hydrolyzed by alkali, so that the aftertreated material cannot be submitted to a soaping or other alkaline treatment.[29] As with formaldehyde aftertreatment, the fastness to light is frequently decreased, and the choice of dyes suitable for aftertreatment with a commercial cation-active agent is based on the production of increased water-fastness without deterioration in light fastness.[30] Dyes derived from 3-sulfosalicylic acid may be submitted to a simultaneous treatment with a copper salt and a cation-active agent.[30a]

Fixanol (ICI), Solidogen (IG), Sapamine (Cb) and Sandofix (S) are examples of products marketed by dye manufacturers for this purpose. Fixanol has been stated to be octadecyl pyridinium bromide;[31] the Sapamines are the hydrochloride, acetate or other salt of oleyldiethylaminoethylamide ($C_{17}H_{33}CONHCH_2CH_2NEt_2$). Solidogen[32] is prepared by chlorinating paraffin wax, m.p. 54-56°, at 100–150° until the chlorine content is 24–26%, corresponding to a trichloroparaffin, which is then heated with 64% of its weight of a polyethylene polyamine for 8 hours at 160–165°. The base is separated by the addition of caustic soda, and converted into the hydrochloride. Solidogen BSE is prepared by methylating Solidogen B in aqueous alkali with dimethyl sulfate.

Numerous types of amines, quaternary ammonium and phosphonium and ternary sulfonium salts have been suggested in patents as reagents for aftertreating cotton and rayon dyed with direct colors. Some examples are: (1) The product obtained by heating ammonium chloride, formalin and acetone at 70°.[33] (2) The product of the action of ammonia on epichlorhydrin is methylated.[34] (3) Triethanolamine is heated with urea till ammonia is no longer evolved, and the product is methylated.[35] (4) The reaction product of β-chloro-β′-hydroxydiethyl ether, octadecylamine, chloroacetic acid and pyridine.[36] (5) A polyethylene polyamine is heated with adipic acid chloride under such conditions that complete acylation of the polyamine does not ensue.[37] (6) Bis-chloroacetyl-*p*-phenylenediamine is heated with pyridine.[38] (7) Tris-*N*-methoxymethylmelamine.[39] (8) The sulfonium salt obtained by heating α-dichlorhydrin with sodium sulfide and alkylating with excess of dimethyl sulfate.[38] (9) Sulfurized phenols heated with *sec.*-aliphatic amines and formaldehyde.[40] Dicyandiamide-formaldehyde condensates improve the wet fastness of direct dyeings on cellulose, and also impart affinity for acid dyes to cellulose.[41] Dyes such as (IX), prepared by heating an azo compound containing a CONH$_2$ group with pyridine hydrochloride and paraformaldehyde can be applied to cotton, and by heating at 115–120° the fastness to washing is increased.[42]

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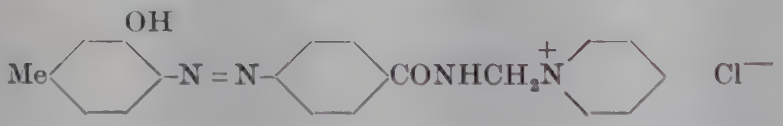
[29] See also Chwala, Martina and Becke, *Melliand Textilber.* **17,** 583 (1937).

[30] See also Ackley, *Am. Dyestuff Reptr.* **29,** 686 (1940); **30,** 148 (1941).

[30a] Sandoz, BP 620,257.

[31] ICI, Barlow and Lawrie, BP 398,175.

[32] *BIOS* **239**; **667.**



(IX)

Topping direct dyes with basic dyes is chemically similar to the treatment with a quaternary ammonium salt; but the object is different. It is either to brighten the shade or to use the direct dye as a mordant for the basic dye.[43]

TREATMENT WITH COPPER SALTS

Copper complexes of azo dyes, of value as fast-to-light direct cotton dyes, have been described earlier.[44] Copper in varying quantities and degrees of permanence in the attachment may also be introduced by treating the dyed fiber with a copper salt, usually copper sulfate (1–3% on the weight of the material) in presence of acetic or formic acid (0.6%) or sodium tartrate at 60° for half an hour. This is an old, inexpensive and well-established method of aftertreating direct dyes with the object of improving light fastness. The increase in the light fastness by coppering is considerable; e.g., from 1 to 4 for Diamine Orange B (with a simultaneous change in shade towards brown); from 4 to 7 for Chrysamine G and R;[11] and from 1 to 5–6 for Benzo Sky Blue. The washing fastness sometimes is also improved. Since the formation of a metallic complex is involved, the dyes must possess the structural requirements of the mordant azo dyes, such as a salicylic acid residue or an *o,o'*-dihydroxyazo group.[44] The constitution of several of the Benzo Fast Copper colors (IG), which dye aftercoppered shades of light fastness 6–7 and washing fastness 4, has now become available.[2, 3, 6] Benzo Fast Copper Yellow GRL is identical with Sirius Supra Yellow FFRL, but standardized to a different strength.[44a] Examples of dyes containing salicylic acid residues are: Benzo Fast Copper Blue GL (5-aminosalicylic acid → Cleve-7-acid → α-naphthylamine → J-acid); Benzo Fast Copper Blue F3GL and Benzo Fast Copper Brown BRL. Examples of *o,o'*-dihydroxyazo dyes are: Benzo Fast Copper Rubine RL (2 moles 6-chloro-2-aminophenol-4-sulfonic acid → X) and Benzo Fast Copper Bordeaux BL (6-nitro-2-aminophenol-4-sulfonic acid → X). Benzo Fast Copper Violet BBL (phenyl-J-acid ← benzidine-3,3'-dicarboxylic acid → 1-naphthol-5-sulfonic acid) and Benzo Fast Copper Violet 3RL are examples of *o*-hydroxy-*o'*-carboxyazo dyes; and a slight variation in this type of structure is represented by

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[33] IG, BP 506,050.

[34] Münz, Keller and Trösken, USP 2,104,092; see also Sandoz, BP 494,625.

[35] Kuhlmann, BP 543,092.

[36] IG, FP 819,000.

[37] IG, DRP 645,882.

[38] IG, BP 460,961; 461,181.

[39] Schreiber, Schroeder and du Pont, USP 2,416,884.

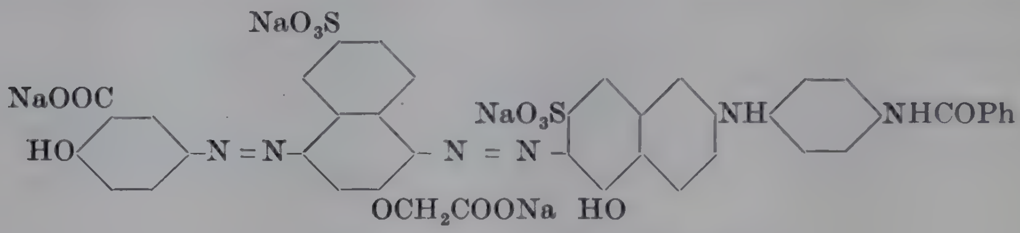
[40] Geigy, BP 511,654; 511,676.

[41] Geigy, BP 594,791; see also Geigy, BP 576,562.

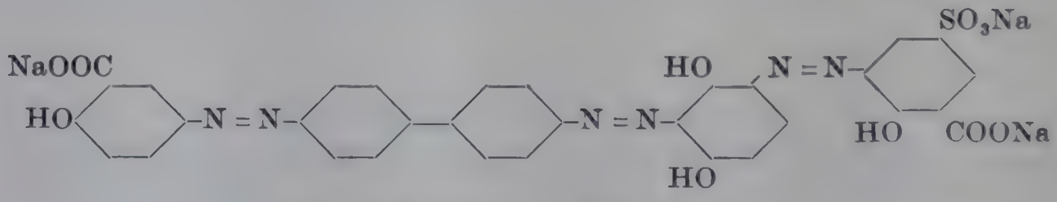
[43] Ciba, SP 216.109.

[43] Latkiewicz, *Melliand Textilber.* 18, 74 (1937).

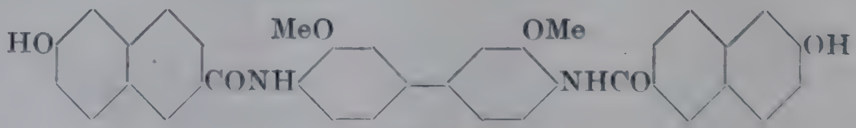
[44] See Chapter XIII.



Benzo Fast Copper Blue F3GL



Benzo Fast Copper Brown BRL



(X)

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[11] See p. 591.

[44] See p. 601.

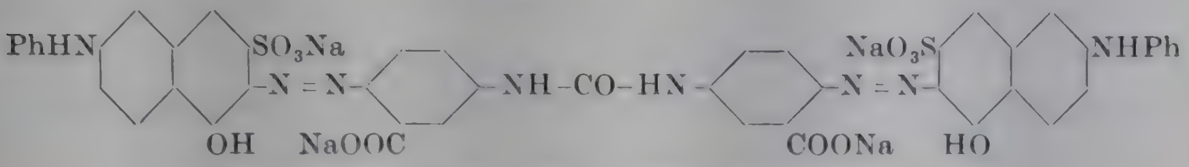
[2] See p. 589.

[3] See p. 589.

[6] See p. 589.

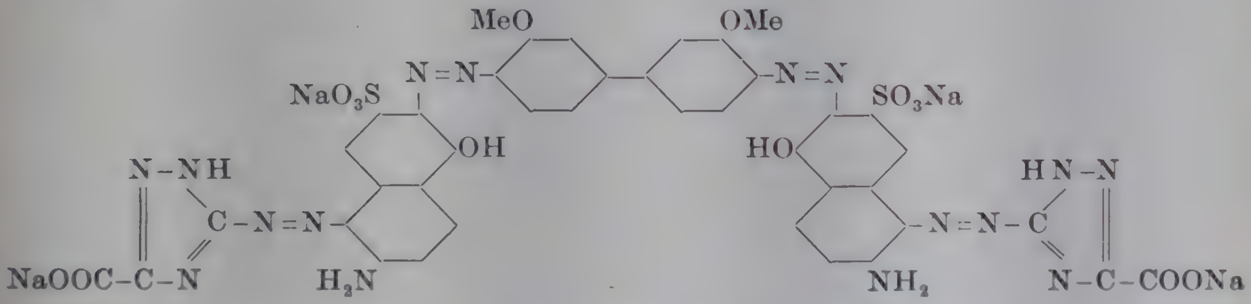
[44a] Benzo Fast Copper Yellow GGL is (4,4'-diaminodiphenylurea-3,3'-dicarboxylic acid ⇉ 2 moles of a mixture of 82.5% acetoacet-*o*-anisidide-4-sulfonic acid and 17.5% acetoacetanilide-4-sulfonic acid); Ref. 2.

Benzo Fast Copper Violet F3BL (5-nitro-2-aminophenoxyacetic acid⟶ *p*-anisyl-J-acid; reduce and phosgenate).



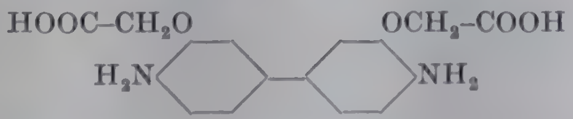
Benzo Fast Copper Violet 3RL

Coppering is recommended for a series of blue direct cotton dyes derived from dianisidine in which there is only one hydroxyl *ortho* to each azo group; the demethylation therefore takes place during metallization.[44] The effect in dyeing is usually to make the shades duller and greener with a simultaneous increase in fastness to light from 1–2 to 6 and a slight increase in fastness to washing. Examples of old dyes of this type are Benzoazurine G (By; CI 502) (NW-acid⟵dianisidine⟶NW-acid), Benzo Blue RW, Diamine Sky Blue FF, Dianil Blue G, Triazol Pure Blue R,[11] and Brilliant Copper Blue GW (Chicago acid⟵dianisidine⟶ phenyl-J-acid).[6] Benzo Fast Copper Navy Blue RL is a recent addition;[6]



Benzo Fast Copper Navy Blue RL

3-amino-1,2,4-triazole-5-carboxylic acid, an intermediate for this dye, is prepared by heating aminoguanidine carbonate with oxalic acid in aqueous solution.[45] Three of the Benzo Fast Copper Blue series are prepared from dianisidine-ω-dicarboxylic acid (XI): Blue FBL (XI⟹2 moles *p*-anisyl-J-



(XI)

acid); Navy Blue BL (benzoyl-J-acid⟵XI⟶2′,4′-dimethoxyphenyl-J-acid); and Navy Blue 3RL (XI⟹2 moles 1-chloro-J-acid).[3, 6] The Cuprofix dyes (S) are for aftercoppering and they cover a range of shades from yellow to black with light fastness 5–7.

Recent patent disclosures consist mainly of salicylic acid derivatives. Examples are red disazo dyes such as (salicylic acid⟵4,4′-diaminobenzanilide⟶benzoyl-J-acid) and brown tetrakisazo dyes such as (sulfanilic acid → *o*-hydroxyacetanilide; saponify → resorcinol ← 4,4′-diaminobenzanilide → salicylic acid).[45a] The tetrakisazo dye (5-aminosalicylic acid → Cleve acid → cresidine → J-acid $\xleftarrow{\text{acid}}$ 5-chloroanthranilic acid) dyes cotton a bluish-gray shade, which turns to a light-fast gray by coppering.[45b] Trisazo dyes (A → M^1 → M^2 → E), such as (XII), in which both A and E contain salicylic acid residues may be applied to cotton by a process in which the dyeing and metallization are carried out simultaneously.[46] For brown shades the dyes are of the type (2-aminophenol-4-sulfonamide → 1,3-dihydroxynaphthalene ← benzidine → salicylic acid).[47] The Coprantines (Cb), of which there are thirty ranging in shade from yellow to green and gray, belong to this class. They are direct cotton dyes which combine with copper salts on the fiber to form stable complexes, the shades having very good fastness to light and good fastness to washing at 75°. The Coprantines are dyed from a weakly alkaline bath; after the dye has been exhausted, copper sulfate and sodium tartrate are added to the same bath, which is heated for a further half hour at 80–90°. It is stated that the Coprantines are distinct in structure from the older aftercoppered direct cotton dyes. The Cuprophenyl dyes (Gy) are of a similar type, applied by a single-bath process.

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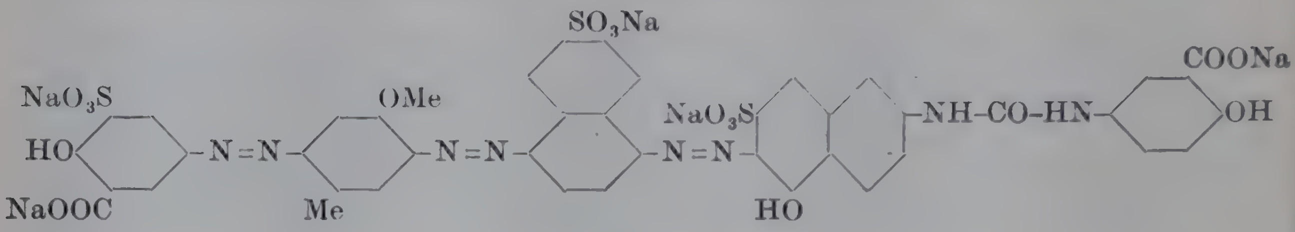
[44] See p. 601. [11] See p. 591. [6] See p. 589. [45] *BIOS* **1153**. [3] See p. 589.



(XII)

By coupling tetrazotized dianisidine with 1-amino-7-naphthol in relatively concentrated caustic potash solution, a dye free from sulfonic groups is obtained, which dyes cotton after-coppered to gray shades.[47a] Disazo and polyazo dyes from tetrazotized (XI), 3-hydroxybenzidine, 3,3′-dihydroxybenzidine and 3-hydroxy-3′-methoxybenzidine[11] are especially suitable for the coppering process if an end component is a 5-pyrazolone; useful red to brownish violet shades are obtained by appropriate choice of other components.[48] The dyes (3,3′-dihydroxybenzidine ⇉ 2 moles J-acid or

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[45a] Ischer and Sandoz, USP 2,472,215; SP 246,185–9. See also Ciba, BP 633,790; USP 2,493,975.

[45b] Bossard and Geigy, USP 2,459,913.

[46] Ciba, BP 455,274; 580,175; 582,977; Kaiser and Ciba, USP 2,435,356; SP 242,995–7.

[47] Ciba, BP 587,110; see also BP 543,100.

[47a] Ciba, BP 616,155.

[11] See p. 591.

[48] IG, BP 518,896; Ciba, BP 572,852; 578,964; 580,486. See also Ciba, SP 229,184; 231,843; 232,503–10; 239,334–41; 244,510–4; USP 2,476,259.

S-acid or 2,6- or 2,7-dihydroxynaphthalene) give fast blue to blue-green shades in conjunction with copper salts by the 1- or 2-bath process.[48a] *o*-Amino-*o*′-carboxyazo dyes, such as the tetrakisazo dyes (dianisidine $\rightrightarrows$ 2 moles of the monoazo dye J-acid $\xleftarrow{\text{acid}}$ anthranilic acid) are rendered fast to washing by aftercoppering without an appreciable change in shade.[49] The trisazo dyes (aminoazo compound $\longrightarrow$ di-J-acid $\longleftarrow$ *o*-aminophenol) exhaust well, and the bright blue shades are appreciably improved in fastness to light, perspiration and wet treatments by coppering.[50] The bluish red disazo dyes ($ArNH_2 \longrightarrow$ *p*-aminobenzoyl-J-acid $\longrightarrow$ 8-hydroxyquinoline) are substantive both to cellulose and protein fibers and are metallizable.[51] Dyeings and prints may be submitted to a simultaneous or successive treatment with a copper compound and a cation-active substance.[51a]

TREATMENT WITH DICHROMATE

Treatment on the fiber with sodium or potassium dichromate (or chrome alum or chromium fluoride) and acetic or formic acid improves the fastness to washing of some direct cotton dyes. The method is an alternative to copper sulfate treatment, and similarly constituted dyes (mainly azosalicylic acids) are suitable for either process; in fact a combination of copper sulfate, dichromate and acetic acid may be employed with advantage for certain dyes (mostly browns and blacks) for the simultaneous improvement of fastness to light and to washing. A few examples, additional to those cited for the copper sulfate method, may be mentioned.

Diamine Fast Red F (salicylic acid $\longleftarrow$ benzidine $\xrightarrow{\text{acid}}$ γ-acid) is suitable for chroming, and the analog from phenyl-γ-acid (alk.), Diamine Brown B (C; CI 423), for the copper chromium treatment. An old and extensively used dye of this type is Benzo Chrome Brown G (By; CI 596) (Diamineral Brown G; C, IG) (salicylic acid $\xleftarrow{2}$ benzidine $\xrightarrow{3}$ *m*-phenylenediamine $\xleftarrow{1}$ sulfanilic acid), which has light fastness 6 after copper-chromium treatment; Benzo Brown D3G extra (IG) is stated to have the same constitution,[2] but its light fastness is only 2–3. Another old and useful dye for cotton as well as wool is Congo Brown G (AGFA; CI 598) (salicylic acid $\xleftarrow{2}$ benzidine $\xrightarrow{3}$ resorcinol $\xleftarrow{1}$ sulfanilic acid); Congo Brown R (AGFA; CI 601) is similarly constituted, but Laurent acid replaces sulfanilic acid. Both Congo Brown G and R are rendered darker, and faster to light and washing, by copper-chromium treatment. Diamine Green G (C; CI 594; *o*-nitroaniline may replace *p*-nitroaniline),[2] applicable to cotton, wool and silk, increases from 1–2 to 2–3 in fastness to washing by chromium fluoride treatment; the light fastness is only 2. Diamine Brown M[11] is suitable both for chroming and for the diazotization-development process. Sirius Supra Brown RT is (salicylic acid ⟵ benzidine ⟶ Cleve acid ⟶ salicylic acid).[52] Sirius Black L (5-aminosalicylic acid ⟶ α-naphthylamine ⟶ γ-acid),[6] which has light fastness 5, increases in washing fastness from 2 to 3 by chroming.

[48a] Ciba, SP 229,184; 238,264; 241,346–7; 246,422–3; USP 2,476,260; BP 631,262. See also BP 636,006; USP 2,475,265.

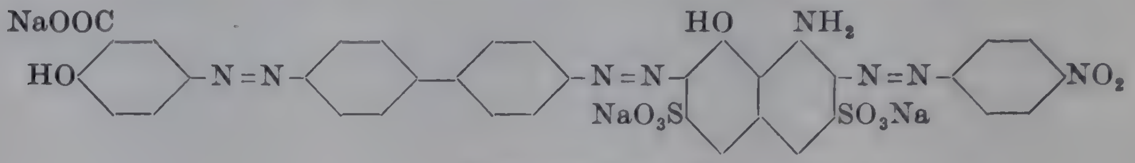
[49] Geigy, BP 579,063; see also BP 594,325; 633,166; SP 238,451–9; 242,497–08; 243,000–2.

[50] Sandoz, BP 592,764.

[51] Anderau, USP 2,411,646; Ciba, SP 237,186; 240,364.

[51a] Ciba, BP 535,582.

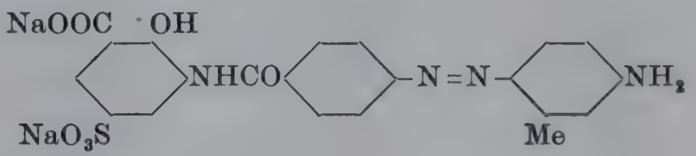
[2] See p. 589.


NaOOC
HO
N=N
N=N
HO
NH2
NaO3S
SO3Na
N=N
NO2

Diamine Green G

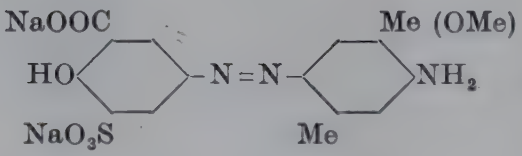
The Benzo (Fast) Chrome dyes (IG) usually contain chromable salicylic acid residues, and the following examples illustrate typical structures.[1] For aftertreatment on the fiber with a mixture of copper and chromium salts, IG have found the two blue dyes (dianisidine $\rightrightarrows$ 2 moles *p*-hydroxy-*m*-carboxyphenyl-J-acid) and (benzidine-3,3′-dicarboxylic acid $\rightrightarrows$ 2 moles J-acid $\rightrightarrows$ 2 moles *p*-hydroxy-*m*-carboxybenzenesulfonyl-J-acid) to be the best products developed to date.[52] Benzo Chrome Black Blue BA is stated to be of a different type, being a derivative of dioxy-S-acid (dioxy-S-acid ⟵ *o*-tolidine $\xrightarrow{\text{alk.}}$ γ-acid ⟶ dioxy-S-acid).[5]

Yellow


NaOOC
OH
NHCO
N=N
NH2
NaO3S
Me

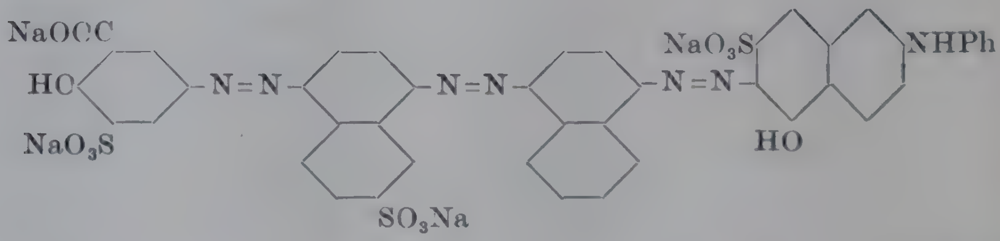
; phosgenate.

Orange Red

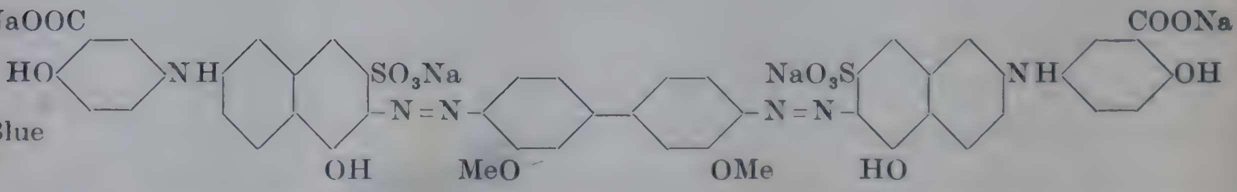

NaOOC
HO
N=N
Me (OMe)
NH2
NaO3S
Me

; condense with dinitrostilbene-disulfonic acid

Blue FG


NaOOC
HO
NaO3S
N=N
N=N
SO3Na
N=N
NaO3S
NHPh
HO

Blue


NaOOC
HO
NH
SO3Na
N=N
OH
MeO
OMe
NaO3S
N=N
HO
NH
COONa
OH

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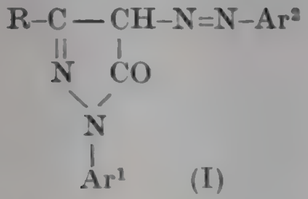
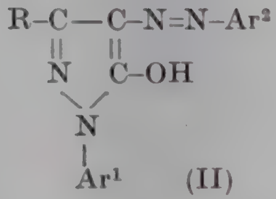
[2] See p. 589.
[11] See p. 591.
[52] *FIAT* **1313**, III.
[6] See p. 589.
[1] See p. 589.
[5] See p. 589.

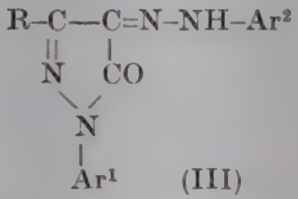
CHAPTER XVIII

PYRAZOLONES

The pyrazolone dyes possess the general structure (I), (II) or (III); (I) and (II) correspond to the keto-enol tautomerism of 5-pyrazolone and 5-hydroxypyrazole, while (II) and (III) correspond to the azo and quinone-hydrazone structures of the azophenols. It is possible to prepare the azo dyes of the pyrazolone series by either of the methods indicated by the azo structures (I) and (II) or the hydrazone structure (III); these are (*a*) coupling 5-pyrazolones with diazonium salts, and (*b*) condensation of one mole of an α, β-diketocarboxylic acid with two moles of an arylhydrazine. However, process (*a*) is the only one now technically employed, so that the pyrazolones fall into line with other azo dyes. The colors obtainable from pyrazolone intermediates are yellow to red, and at one time the special value of the pyrazolones was in the production of yellow pigments and dyes, but their uses have now been extended to red and bluish-red dyestuffs, notably in the chrome color class.[1-6] Good fastness to light is a characteristic of the pyrazolone dyes and pigments, and several of the acid and acid-mordant dyes are also noted for their high fastness to severe wet treatments.







The soluble azo dyes derived from pyrazolone are mainly acid colors, of which a few have mordant dyeing properties. Substantivity for cotton can be produced by a suitable choice of the diazonium component, the pyrazolone ring itself being a favorable factor, and pyrazolone dyes applicable to cellulose fibers are receiving increasing attention. The insoluble dyes of the series are of value as pigments (see Chapter XXII).

PHENYLHYDRAZINE DERIVATIVES

Phenylhydrazine, its *p*-sulfonic acid and other derivatives are important intermediates for the preparation of the corresponding pyrazolones. Examples are 2-chloro-6-methylphenylhydrazine-4-sulfonic acid (I), the

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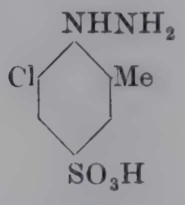
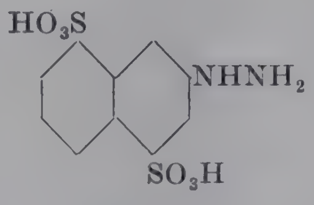
[1-6] As in Chapter XII.

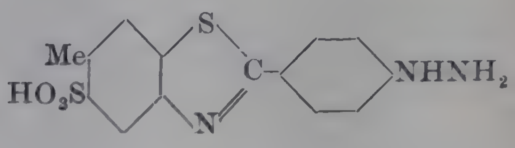
naphthylhydrazine (II), the hydrazine from J-acid, and the dehydrothiotoluidine derivative (III). They can be prepared by a general method


NHNH2
Cl
Me
SO3H

(I)

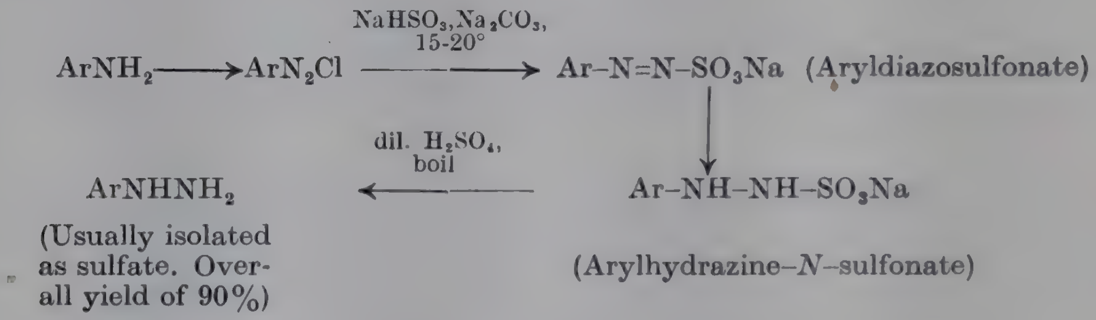

HO3S
NHNH2
SO3H

(II)


Me
HO3S
S
C
N
NHNH2

(III)

of reduction of the appropriate diazonium salt, via the diazosulfonate, by means of neutral sodium sulfite solution.[7, 8] In some cases it is preferable to


ArNH2
ArN2Cl
NaHSO3,Na2CO3, 15-20°
Ar–N=N–SO3Na (Aryldiazosulfonate)
Ar–NH–NH–SO3Na
(Arylhydrazine–N–sulfonate)
dil. H2SO4, boil
ArNHNH2
(Usually isolated as sulfate. Overall yield of 90%)

use stannous chloride or zinc dust and acetic acid as the reducing agent.

DERIVATIVES OF 1-PHENYL-5-PYRAZOLONE-3-CARBOXYLIC ACID

Tartrazine (Ziegler, 1884; CI 640) is still largely employed as an acid dye for wool with good leveling and moderate fastness properties. Its poor fastness on silk is noteworthy, since wide differences in the fastness of the same dye on wool and silk are not common, although many dyes exhibit greater fastness on wool than on cotton. Ziegler discovered two routes to Tartrazine of which only the second is now employed in technical practice. (*a*) Two moles of phenylhydrazine-*p*-sulfonic acid are condensed with one mole of dihydroxytartaric acid (I) reacting as diketosuccinic acid (II). The dye made from a mixture of phenylhydrazine *o*- and *p*-sulfonic acids is marketed as Fast Supra Yellow 2G (IG).[5] (*b*) The pyrazolone skeleton (III) is first synthesized by condensing oxalacetic ester with one mole of phenylhydrazine-*p*-sulfonic acid. Oxalacetic ester is prepared by condensing ethyl oxalate with ethyl acetate and sodium in benzene, and used

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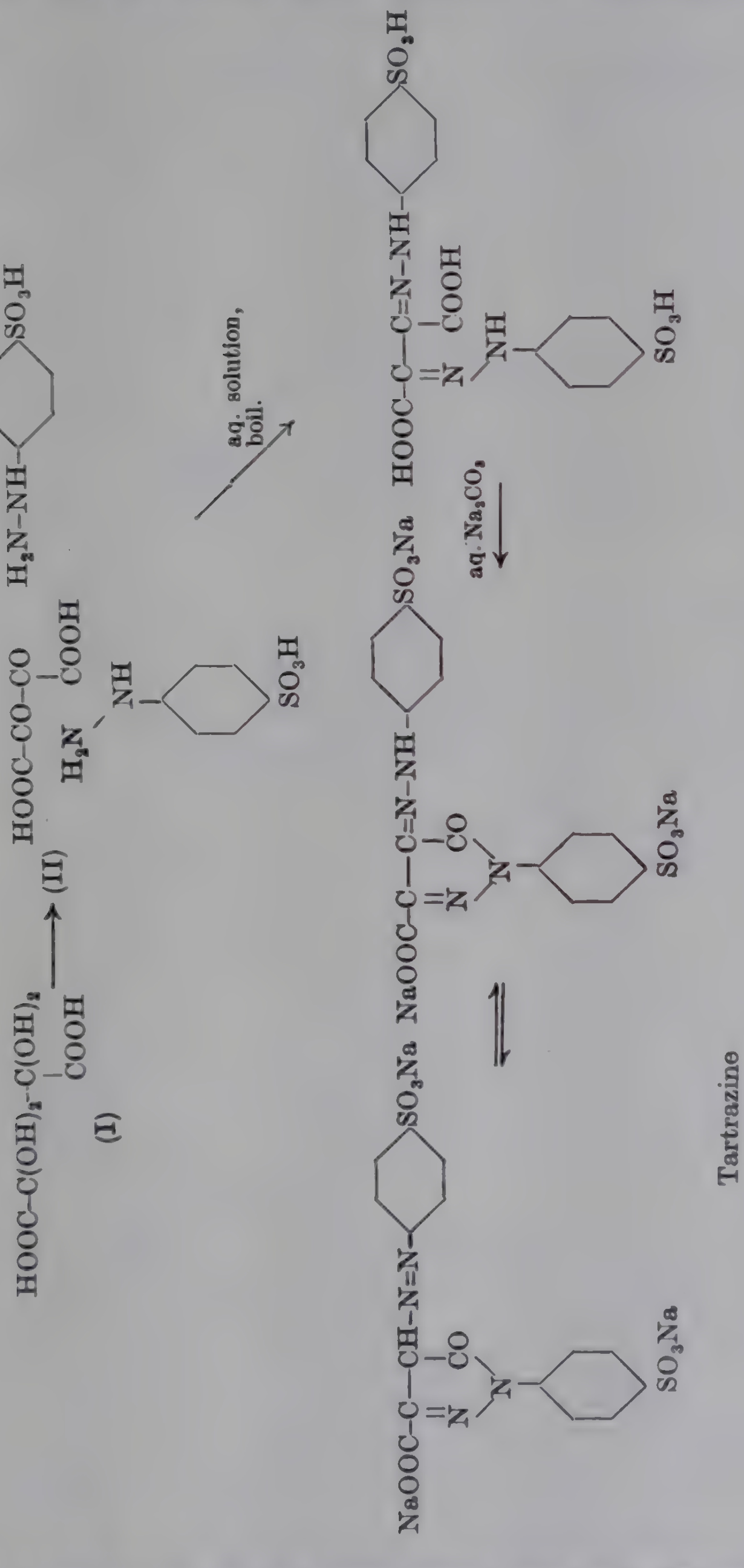
[7] Technical details for the preparation of a large number of arylhydrazines and 1-aryl-5-pyrazolones are described in *BIOS* **986**.

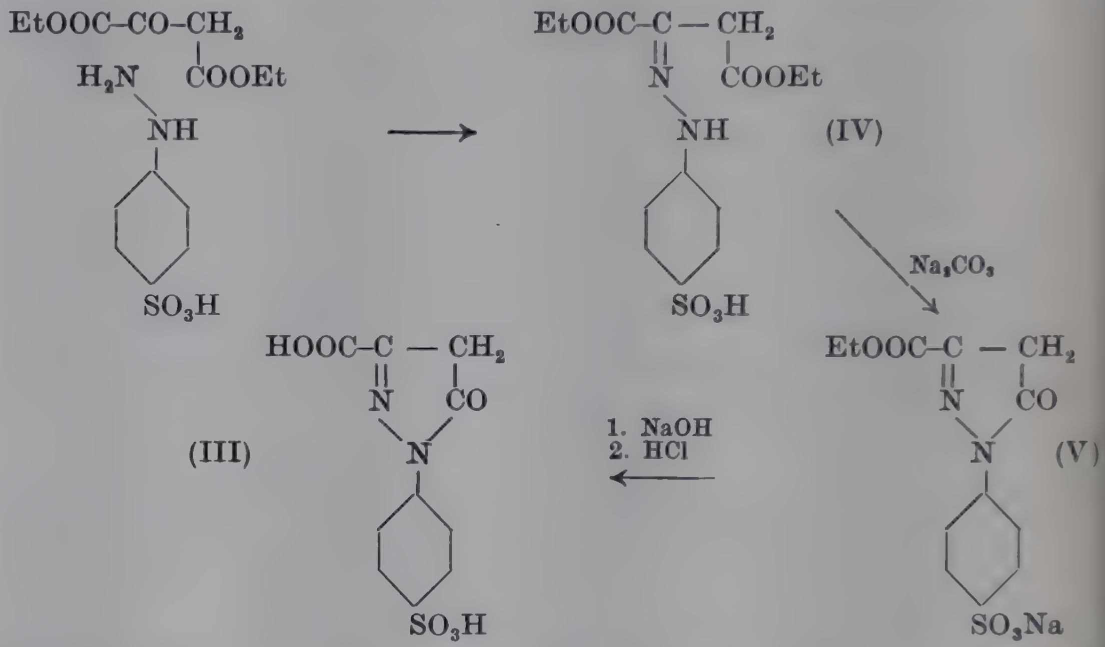
[8] Coleman, *OSCV* I, p. 442.

[5] See p. 607.

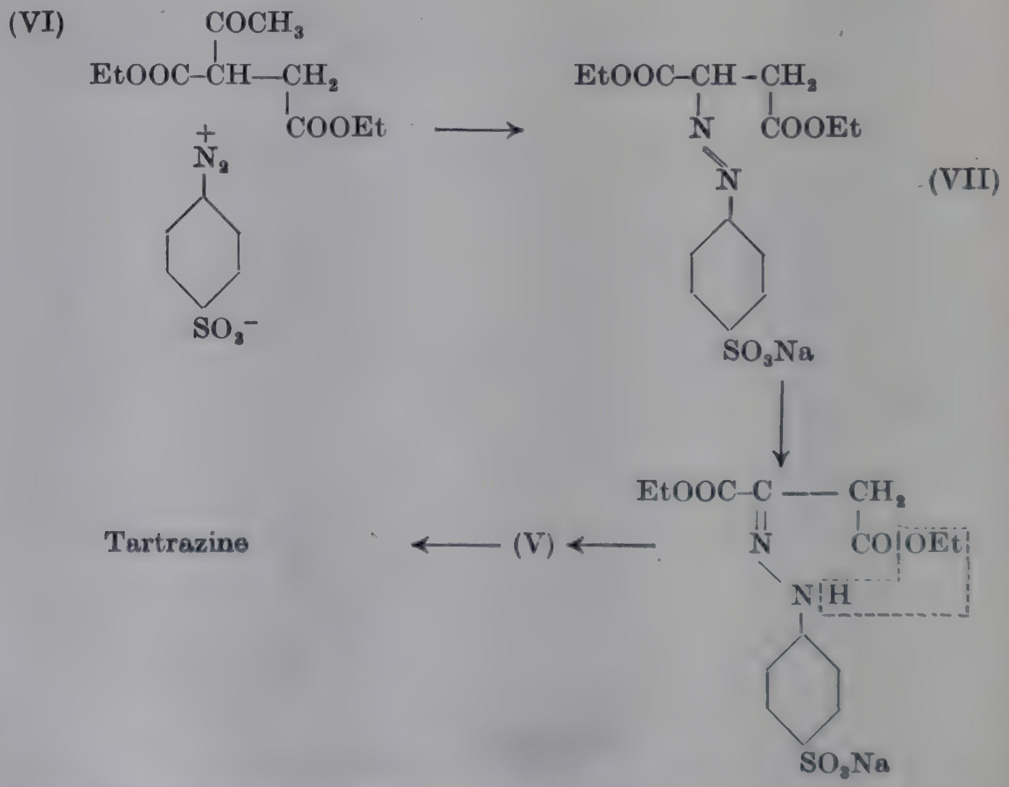
in the form of the sodium salt. At a temperature of about 75° the formation of the hydrazone (IV) is almost instantaneous. Cyclization of (IV) to the


HOOC-C(OH)₂-C(OH)₂
COOH
(I)
(II)
HOOC-CO-CO
COOH
H₂N
NH
SO₃H
H₂N-NH-
SO₃H
aq. solution,
boil.
HOOC-C—C=N-NH-
N
COOH
NH
SO₃H
SO₃H
aq. Na₂CO₃
NaOOC-C—C=N-NH-
N
CO
N
SO₃Na
SO₃Na
NaOOC-C—CH-N=N-
N
CO
N
SO₃Na
SO₃Na
Tartrazine

pyrazolone and hydrolysis of the ester group are both effected by caustic soda solution; but if the ester (V) is desired, sodium carbonate is used for cyclization. In preparing other 1-aryl-5-pyrazolone-3-carboxylic acids by the same method, isolation of the carboxylic acid (III) may mean a drop in the yield, and the sodium salt may then be used directly for coupling. Tartrazine is prepared by coupling (III) with diazotized sulfanilic acid.[1]


EtOOC–CO–CH$_2$
H$_2$N
COOEt
NH
SO$_3$H
EtOOC–C—CH$_2$
N
COOEt
NH
(IV)
SO$_3$H
Na$_2$CO$_3$
EtOOC–C — CH$_2$
N
CO
N
(V)
SO$_3$Na
1. NaOH
2. HCl
HOOC–C — CH$_2$
N
CO
N
(III)
SO$_3$H

Kendall and Fry have described a new synthesis of pyrazolones and derived azo dyes.[9] When diethyl 2-acetylsuccinate (VI) is treated with


(VI)
COCH$_3$
EtOOC–CH—CH$_2$
COOEt
$\overset{+}{N_2}$
SO$_3^-$
EtOOC–CH–CH$_2$
N
COOEt
N
(VII)
SO$_3$Na
EtOOC–C —— CH$_2$
N
CO OEt
N H
SO$_3$Na
Tartrazine
(V)

at least two moles of diazotized sulfanilic acid in alkaline solution, and the product salted out and hydrolyzed by means of boiling 2.5 *N* caustic soda solution, Tartrazine separates on cooling.[9] The first stage is coupling with the elimination of the acetyl group to form (VII), which rearranges and cyclizes to (V).

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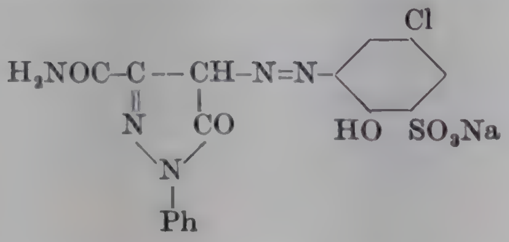
[1] See p. 607.

[9] BP 585,780–1; USP 2,457,823.

Kiton Yellow S (Cb; CI 637) (Aniline⟶III) is more level dyeing than Tartrazine. Tartrazine GGX (IG) (*o*-toluidine disulfonic acid⟶1-[2′-methyl-3′,5′-disulfo]phenyl-5-pyrazolone-3-carboxylic acid) is more soluble than Tartrazine (Tartrazine 0).[4] Wool-Silk Yellow G (IG) is (*o*-chloroaniline ⟶V).[4] The Fast Light Yellows are useful acid dyes with good leveling and fastness properties. The GGT and 3G brands (IG) are prepared by coupling diazotized orthanilic acid with (III) and with the *o*-sulfophenyl isomer respectively.[4] The cyclohexylamine salt of the dye (3-chloro-*o*-toluidine⟶2′-chloro-6′-methyl-V), admixed with 10% of phenyl *p*-toluenesulfonate for improving the solubility, is marketed as Zapon Fast Yellow C for use in coloring lacquers.[10] Normal Yellow 3GL (MLB; CI 644) (*m*-4-xylidine-5-sulfonic acid⟶III) dyes a greener yellow than Tartrazine and is faster to light.

A mordant dye in which a 5-pyrazolone-3-carboxyamide is used as second component is Acid Alizarin Bordeaux B (IG).[1] The isomer from



Acid Alizarin Bordeaux B

6-chloro-2-aminophenol-4-sulfonic acid is Acid Alizarin Red GN (IG).[4] These are level dyeing dyes with moderate fastness properties applied by the afterchrome method. When a 4-substituted 2-aminophenol-6-sulfonic acid is diazotized and coupled with 1-phenyl-5-pyrazolone-3-carboxyamide, the dyes, applied to wool by the chromate process, give bordeaux shades, fast to light, milling and potting.[11]

Saturn Yellow GG (IG) (3-chloro-*o*-toluidine⟶2′-chloro-6′-methyl-V) and 5GL (IG) (aniline-2,5-disulfonic acid⟶1-[2′,5′-disulfo]phenyl-5-pyrazolone-3-carboxylic acid) are useful for lake making.[4] Saturn Yellow 3G (B) is prepared by the condensation of 3-chloro- or 3-bromotolyl-2-hydrazine-5-sulfonic acid with dihydroxytartaric acid.[12]

The direct cotton color, Toluylene Yellow RL (IG), is stated[6] to be (*N*-*p*-aminobenzoyl-*p*-aminobenzeneazosalicylic acid⟶III); and Benzo Light Orange G (IG) to be[4] the disazo dye (salicylic acid⟵benzidine⟶

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[9] See p. 610.

[4] See p. 607.

[10] *FIAT* 1313, III.

[1] See p. 607.

[11] Beech, Mendoza and ICI, BP 587,334.

[12] Fierz-David, Künstliche Organische Farbstoffe, Ergänzungsband, Springer, Berlin, 1935.

[6] See p. 607.

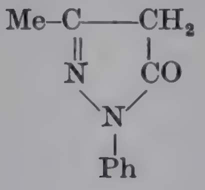
mixture of III and the 3-methylpyrazolone from 2-naphthylamine-5,7-disulfonic acid). Pyrazol Orange (S; CI 653) (salicylic acid←—benzidine—→III) has light fastness of only 3–4, but finds use in dyeing and printing cotton and in dyeing unions.

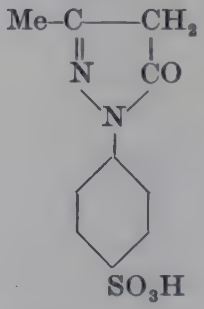
Dyes such as (2-nitro-4-thiocyanoaniline—→V) are useful dyes for cellulose acetate.[13]

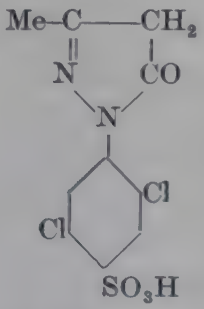
DERIVATIVES OF 1-PHENYL-3-METHYL-5-PYRAZOLONE

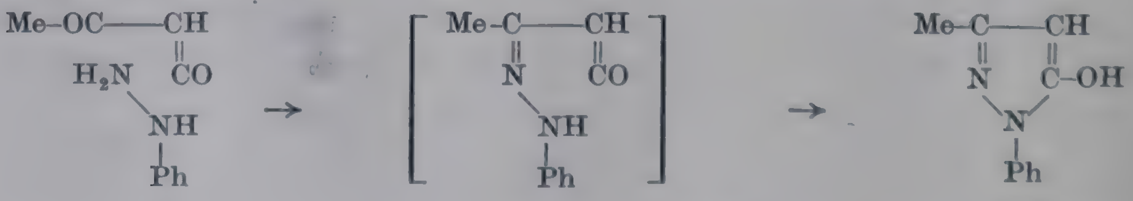
The more recent pyrazolone intermediates are nearly all derived from ethyl acetoacetate; they have the general form (I), and various azo dyes are obtained by introducing suitable substituents into the 1-phenyl ring and the aryl group of the diazonium component with which (I) is coupled.

The general method of preparation of 1-aryl-3-methyl-5-pyrazolones is the condensation of acetoacetic ester with the appropriate arylhydrazine. The 1-phenyl compound (I) is manufactured in large quantities as a dye intermediate and for the production of antipyrine by methylation. When ethyl acetoacetate and phenylhydrazine in a small amount of aqueous alcohol are agitated, first below 50° and finally at the boil for a few hours, the pyrazolone crystallizes out on cooling, and after washing with alcohol it may be used without further purification. The yield is 93% on the hydrazine. For the sulfonated compounds, aqueous solutions of the sodium salts prepared by careful neutralization of the arylhydrazine sulfonic acids are employed. Three important intermediates for pyrazolone dyes are (I) and its *p*-sulfo- and 2′,5′-dichloro-4-′sulfo-derivatives (II and III).


(I)


(II)


(III)


(I)

An alternative method for the preparation of pyrazolones is to condense diketene with arylhydrazines in boiling benzene.[14] However, if one mole of diketene is condensed with two moles of phenylhydrazine at low temperature, the phenylhydrazone (IV) of acetoaceticphenylhydrazide (V) is formed. On heating (IV) with concentrated mineral acid, it undergoes hydrolysis

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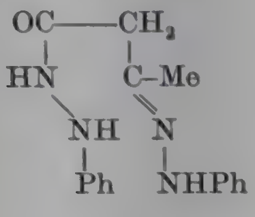
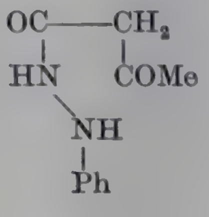
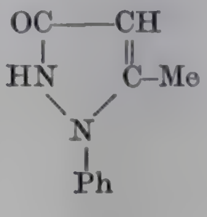
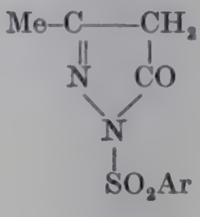
[13] Strain, Dickey and Eastman Kodak, USP 2,430,484.

[14] Johnson, USP 2,017,815; see also IG, BeP 450,727.


(IV)


(V)

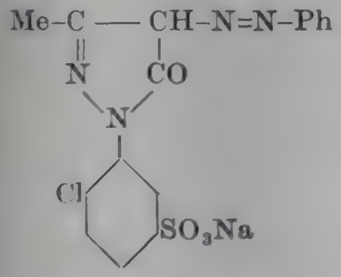

(VI)

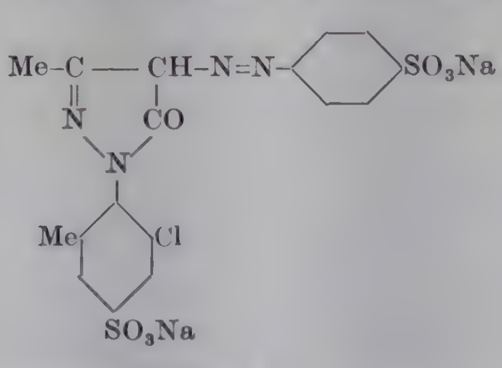

(VII)

to (V) and then cyclization to 1-phenyl-5-methyl-3-pyrazolone (VI).[15] Although (VI) couples with diazonium salts more slowly than the 5-pyrazolone (I), it can be used as an intermediate for azo dyes.[16]

A series of *p*-nitro-, acetamido- and amino-1-arylsulfonyl-3-methyl-5-pyrazolones (VII) have been prepared by treating pyrazolones with a free 1-position with a *p*-nitro- or *p*-acetamidoarylsulfonyl chloride in a solvent, and reducing the nitro group or hydrolyzing the acetamido group.[17]

Acid dyes. Fast Light Yellow G (By; CI 636) (Aniline⟶II), Xylene Fast Yellow 2G (S; CI 639) (sulfanilic acid⟶III), Wool Fast Yellow 3GL (IG), and Fast Light Yellow EGG (IG) (sulfanilic acid⟶2′-chloro-5-′sulfo-I), Fast Light Yellow X or E3G (IG) (Tobias acid⟶2′-chloro-4′-sulfo-6′-methyl-I) and Anthralan Yellow G[1, 5] are largely used acid colors with high fastness to light (6–7). Xylene Fast Yellow 2G (Xylene Light Yellow) is valued for its brightness, level dyeing character and fastness to light; and among the pyrazolone intermediates for acid colors, (III) is probably the most important. Supramine Yellow S (IG) uses the same pyrazolone component as Fast Light Yellow EGG, the diazonium component being 2-naphthylamine-1-sulfonic acid.[4] Hydrazine Yellow RL (IG) is (4-chloroaniline-3-sulfonic acid⟶I).[4]


Wool Fast Yellow 3GL


Anthralan Yellow G

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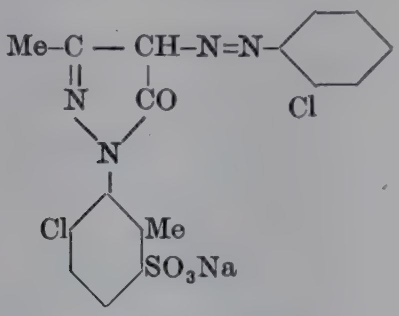
[15] Lecher, Parker and Conn, *JACS* **66**, 1959 (1944).

[16] Lecher *et al.*, USP 2,227,654; Nies and American Cyanamid, USP 2,432,034.

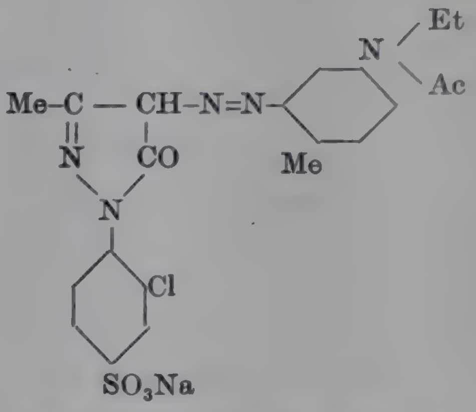
[17] American Cyanamid, USP 2,243,324.

[1] See p. 607.   [5] See p. 607.   [4] See p. 607.

Flavazine E3GL (IG) is a very level-dyeing wool dye, yielding yellow shades of high light fastness. Flavazines L, S and 4G are prepared by coupling benzenediazonium chloride with 1-phenyl-5-pyrazolones containing 4′-sulfo-3-methyl, 4′-sulfo-3-carboxyl, and 2′-chloro-4′-sulfo-6′-methyl-3-carboxyl groups respectively. The influence of an acetamido group in imparting good leveling property is illustrated in Supramine Yellow 3G (IG).

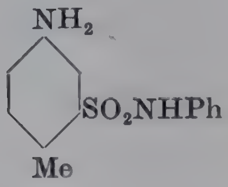


Flavazine E3GL

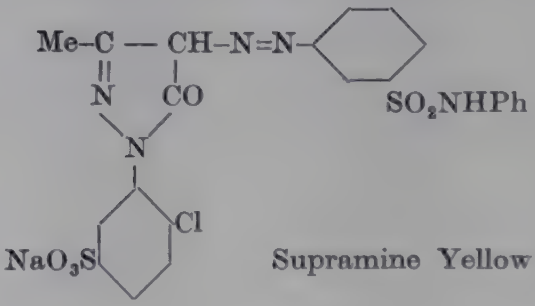


Supramine Yellow 3G

Supramine Yellow R (IG) (VIII⟶II) is a wool dye which is very level dyeing, but has only moderate light fastness. Supramine Yellow 3GL (IG) is both level dyeing and fast to light (6–7).[4]



(VIII)



Supramine Yellow 3GL

Sulphon Yellow R (IG) (benzidine-2,2′-disulfonic acid⟹two moles I) is an acid dye with good fastness to light (5) and milling (3–4).[2] Azo Milling Yellow R (IG) (salicylic acid⟵*m*-tolidine⟶2′-methyl-II) is a typical milling color, which also possesses high light fastness (5–6).[4] Milling Yellow HG (IG) (4,4′-diaminotriphenylmethane⟹two moles II) is a wool dye with very high wash fastness and good light fastness (5). The analog from 2′-chloro-6′-methyl-II is Milling Yellow H3G (IG), a greener yellow.[4]

Among recent patents on this group of dyes, a few may be mentioned. Fast yellow dyes for wool and silk are prepared by coupling a diazotized mono-*N*-acyl-*p*-phenylenediamine with a 1-sulfophenyl-3-alkyl-5-pyrazolone; the acyl group may be benzoyl or benzenesulfonyl.[18] Greenish-yellow dyes such as (p-$C_{15}H_{31}$–CONH–SO_2–C_6H_4–NH_2⟶III) are fast to milling and light.[18a] All-round fastness is claimed for the yellow to orange dyes ($H_2N–C_6H_4–SO_2NHSO_2–Ar \longrightarrow$pyrazolone free from SO_3H).[18b] Special fastness and exhausting properties are claimed for the yellow dyes obtained by coupling sulfonic acids of aminophenoxydiphenyl or aminodiphenyl ether with a 5-pyrazolone in which the 1-phenyl contains two chlorine atoms.[19] Supranol Yellow 4G, which the IG had made experimentally and were planning to market,[3] has good affinity from a neutral bath, and is similar in its dyeing and wet fastness properties to Carbolan Yellow 3GS (ICI); the light fastness is only moderate (4–5).

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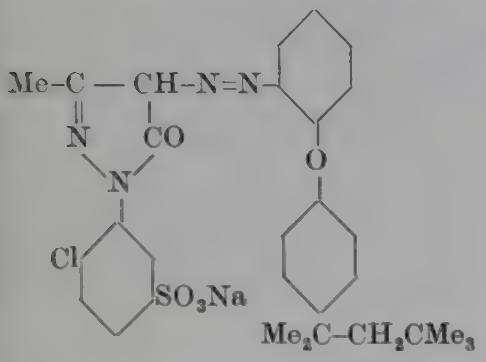
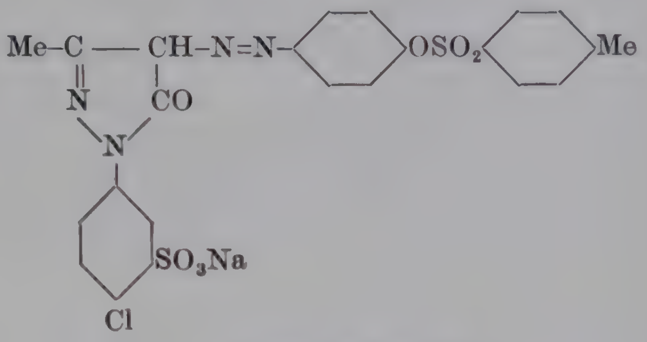
[4] See p. 607.

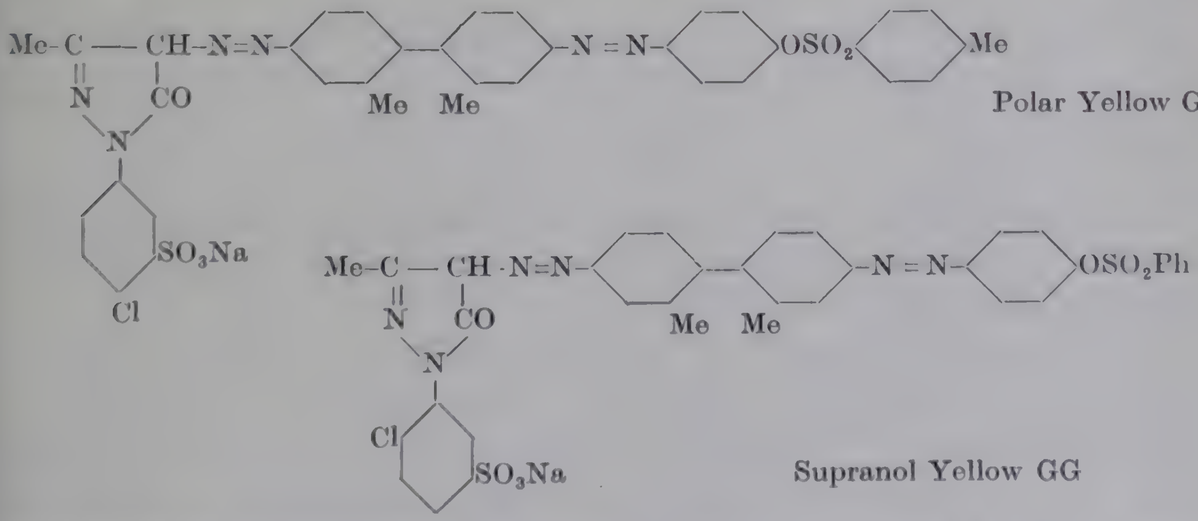
[2] See p. 607.

[18] Sandoz, BP 525,834.


Supranol Yellow 4G


Polar Yellow 5G

The Polar colors are acid colors fast to milling, and they have the common feature of a *p*-toluenesulfonyl group. Two examples are Polar Yellow 2G (*p*-aminophenol⟶II; acylate the phenolic hydroxyl with *p*-toluenesulfonyl chloride) and 5G (Gy; CI 642). Polar Yellow G (Gy)[12] and Supranol Yellow GG (IG)[4] are disazo dyes from *m*-tolidine, which leads to dyes unsubstantive to cotton. Sulphon Orange G (By) (I⟵benzidine-2,2′-disulfonic acid⟶β-naphthol)[6] has milling fastness 4, but light fastness only 2–3.

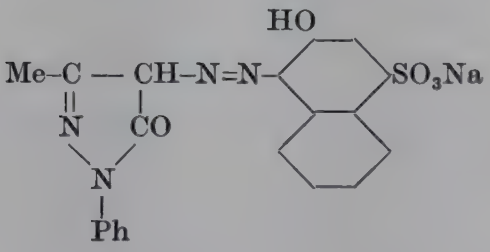

Polar Yellow G

Supranol Yellow GG

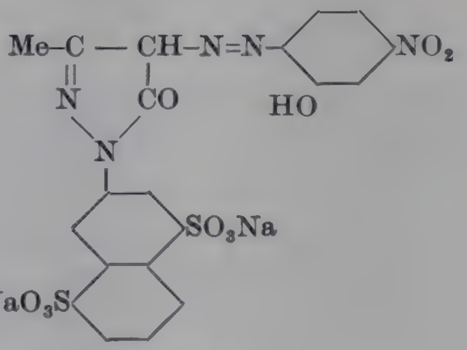
[18a] Sandoz, SP 243,003–7. See also BP 597,131. [18b] Geigy, BP 621,642.
[19] Geigy, BP 520,101. [3] See p. 607. [12] See p. 611. [4] See p. 607. [6] See p. 607.

Some of the acid pyrazolone dyes are useful for dyeing leather, and an example is Igenal Yellow RR (IG) (*o*-chloroaniline→2′-sulfo-I).[5, 20]

Mordant dyes. If the diazonium salt is prepared from an *o*-aminophenol, the dye is applicable as a mordant color, or it may be used for the preparation of a soluble metallic coordination complex in substance.[21] Chrome Orange LR (By) (2-aminophenol-4-sulfonic acid→I)[6] has light fastness 7 and milling fastness 4. Acid Alizarin Red G (IG) (4-methyl-2-aminophenol-6-sulfonic acid→I) is a chrome-developed wool dye,[4] with light fastness 6 and milling fastness 5. Eriochrome Red B (Gy; CI 652) (Salicine Bordeaux G, IG)[4] has long been valued as a wool color, the dull orange shade first obtained changing to a brilliant and much faster crimson shade by afterchroming; the light fastness is good, but not excellent according to modern standards. The preformed chromium complex of this dye (Neolan Red B) was one of the first members of the Neolan series.[12]



Eriochrome Red B



Diamond Red G

Anthracene Chrome Red B (IG) is the 4-sulfophenyl analog of Eriochrome Red B. Acid Alizarin Red 3B (Salicine Bordeaux R) (IG) (6-chloro-1-amino-2-naphthol-4-sulfonic acid→I)[2] is a chrome mordant dye, applicable by any of the chroming methods. Diamond Red G (IG) is an afterchrome color with very good light fastness.[4] Acid Anthracene Brown KE (By) (5-chloro-4-nitro-2-aminophenol→mixture of II and 1-naphthol-5-sulfonic acid)[6] has light fastness 7 and milling fastness 5.

Acid Alizarin Flavine R (IG) (anthranilic acid→II) is a chrome-developed dye for wool with very high light fastness (7). Acid Alizarin Flavine GF (IG) is a mordant dye containing two metallizable groups: an *o*-hydroxy-*o*′-carboxyazo group and a salicylic acid residue.[1, 4] Pigment Fast Yellow G (MLB, 1903; CI 651) (4-sulfoanthranilic acid→I) and Pigment Fast Yellow R (*o*-toluidine-5-sulfonic acid→I)[12] are used for making lakes.

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[5] See p. 607.

[20] Mendoza and ICI, BP 596,109.

[21] See Chapter XIII.

[6] See p. 607.

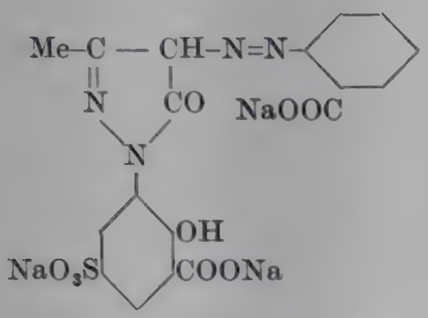
[4] See p. 607.

[12] See p. 611.

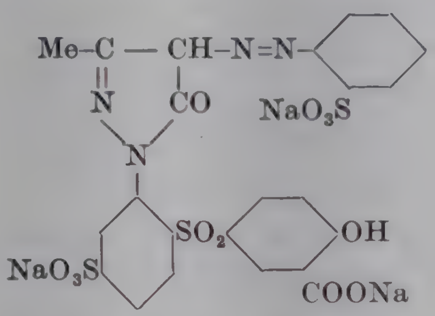
[2] See p. 607.

[1] See p. 607.

Acid Chrome Yellow 3GL (IG) and the similar dye Chrome Yellow 2GL (IG) using *p*-toluidine as the diazonium component[1, 4] have very high light fastness (7); the significant factor apparently is the arylsulfone group attached to the 1-phenylpyrazolone. Acid Chrome Yellow GL (IG)[4] (IX⟶2′-chloro-5′-sulfo-I) is also a fast chrome-developed wool color; its mordanting properties involve the *o*-hydroxysulfonamide group.

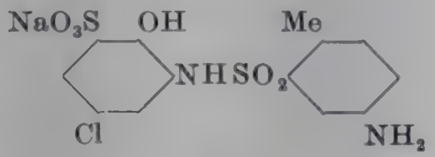


Acid Alizarin Flavine GF

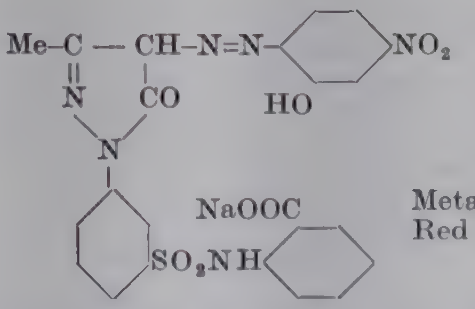


Acid Chrome Yellow 3GL

Mordant colors applicable by a single bath or metachrome process[21] have been prepared from 5-pyrazolones. Metachrome Red 5G (IG) (4-chloro-2-aminophenol-6-sulfonic acid⟶I) and Metachrome Red BB (IG) are two examples.[4, 22] Metachrome Red 5G has excellent fastness properties (light 6–7, milling 4–5).



(IX)



Metachrome Red BB

Applied by single bath or afterchrome methods, good light fastness is claimed for the yellowish to bluish red dyes prepared by coupling a diazotized 2-aminophenol-6-sulfonic acid, containing in the 4-position an alkyl or cycloalkyl group of C_3 to C_8, with a 5-pyrazolone not containing sulfonic or carboxyl groups.[23] The red dye (*o*-aminophenol-*p*-sulfonamide ⟶1-aryl-3-methyl-5-pyrazolone free from SO_3H) gives on chroming on the fiber a pure orange shade with good light fastness.[23a] When the diazo-oxide of 3,6-dichloro-2-aminophenol-4-sulfonic acid, obtained from 2,4,5-trichlorometanilic acid, is coupled with 3′-sulfo-I and converted into a chromium complex, the dye has excellent leveling and fastness properties.[24] Among the pyrazolones more recently suggested as second components for

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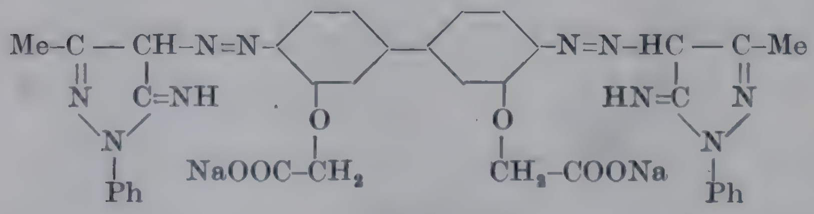
[1] See p. 607.
[4] See p. 607.
[21] See p. 616.
[22] Contrast *BIOS* 271.
[23] Geigy, BP 584,255.
[23a] Ciba, SP 228,935.
[24] Carson and du Pont, USP 2,421,315; 2,443,226.

the preparation of metachrome colors is 1-phenoxyphenyl-3-phenyl (or methyl)-5-pyrazolone. High fastness properties and strength of shade are claimed for the monoazo, single-bath chrome dyes for wool prepared from the usual *o*-aminophenol type of first component coupled with a 1-phenyl-5-pyrazolone in which the phenyl carries a *p*-phenoxy group. The pyrazolone is prepared from the hydrazine obtained by reduction of diazotized *p*-aminodiphenyl ether.[25] 1-(*o*- or *p*-)-Xenyl-3-phenyl (or methyl)-5-pyrazolone, coupled with diazotized *o*-aminophenol derivatives, gives orange-brown, single-bath mordant dyes for wool with good all-round fastness.[26] Mordant dyes yielding orange chrome complexes are obtained by coupling diazotized 4-amino-5-pyrazolones with β-naphthol.[27]

Direct cotton dyes. By using a *p*-diamine, Primuline, etc., as the first component, or by linking up two arylazo-pyrazolone units containing amino groups by means of phosgene or cyanuric chloride, the pyrazolone series have been extended to include several direct cotton dyes. Dianil Yellow R (MLB; CI 649) (Primuline⟶I) is useful for wool and silk, as well as the cellulose fibers. In preparing direct cotton dyes of this series from a tetrazotized diamine of the benzidine type, it is usual to employ one mole of a pyrazolone and one mole of a second substance as coupling components. An example is Benzo Fast Orange G (IG), a dye[2] with moderate light fastness; it has the constitution: salicylic acid⟵benzidine⟶a mixture of (*m*-sulfo-I) (25%) and 1-(5′,7′-disulfo-2′-)naphthyl-3-methyl-5-pyrazolone (75%). Toluylene Fast Orange GL (salicylic acid⟵benzidine⟶pyrazolone from 2-naphthylamine-4,6-disulfonic acid)[6] has light fastness 5. These salicylic acid derivatives have very good dischargeability. Several of the Benzo Fast Copper dyes[28] are pyrazolone derivatives. Examples are Benzo Fast Copper Yellow RLN (acetoacetanilide⟵4,4′-diaminodiphenylurea-3,3′-dicarboxylic acid⟶3′-sulfo-I); Benzo Fast Copper Red RL (6-nitro-1-diazo-2-naphthol-4-sulfonic acid⟶4′-amino-I; phosgenate);[6] Benzo Fast Copper Red 2GL; Benzo Fast Copper Brown TL (I⟵benzidine-3,3′-



Benzo Fast Copper Red 2GL

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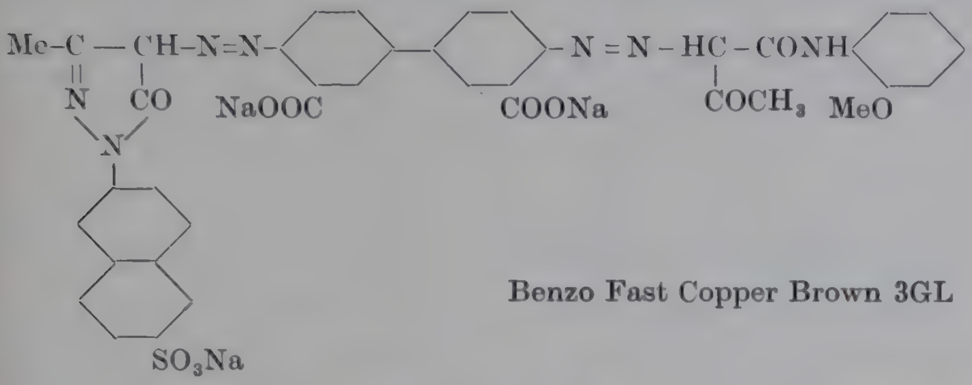
[25] Beech, Mendoza and ICI, BP 561,516; 624,247; USP 2,429,600.

[26] Beech, Mendoza and ICI, BP 560,892.

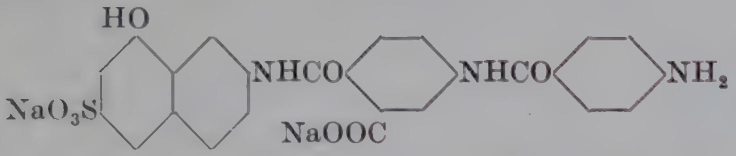
[27] Nies, USP 2,420,791. For other examples of metallizable pyrazolone dyes, see Ciba, USP 2,494,416; Geigy, USP 2,494,969; BP 627,069; 629,412.

[2] See p. 607. [6] See p. 607. [28] See Chapter XVII.

dicarboxylic acid → 6-sulfo-2,8-dihydroxynaphthalene-3-carboxylic acid);[3] Benzo Fast Copper Brown 3GL;[4] and Benzo Fast Copper Brown TRL (I ← benzidine-3,3′-dicarboxylic acid → X).[10] 1-Phenyl-3-methyl-5-aminopyrazole, required for Benzo Fast Copper Red 2GL, is prepared by dimerizing acetonitrile with sodium and condensing diacetonitrile with phenylhydrazine.[3]



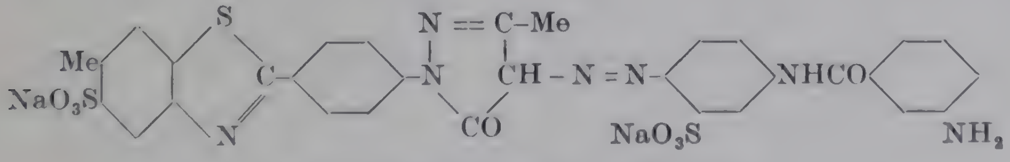
Benzo Fast Copper Brown 3GL



(X)

The copper complexes of the dyes (bis-4-amino-3-carboxyphenyl-urea $\rightrightarrows$ two moles of a pyrazolone containing a sulfonamide group) are fast to light, washing and acid.[29] Copper complexes with good affinity for cotton and excellent light fastness are obtained from monoazo dyes such as (one mole 6-nitro-1-amino-2-naphthol-4-sulfonic acid → bis-pyrazolone from diaminodiphenylurea).[29a] 3,3′-Dihydroxybenzidine is a suitable diazonium component for metallizable pyrazolone dyes.[29b]

In Diazo Brilliant Orange 5G extra (IG), high cotton affinity is secured by using a pyrazolone prepared from dehydrothiotoluidinesulfonic acid, and as diazonium component *m′*-nitrobenzoyl-*p*-phenylenediaminesulfonic acid.[4] Diazotized on the fiber and developed with β-naphthol,[28] the shades have low fastness to light (3), but because of their brightness and moderate fastness to washing (3) the dye is used. Another interesting method of



Diazo Brilliant Orange 5G extra

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[3] See p. 607.

[4] See p. 607.

[10] See p. 611.

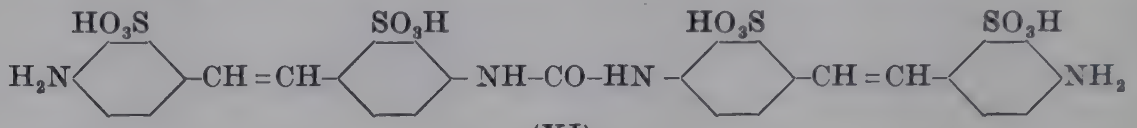
[29] Pieth and Ciba, USP 2,427,534.

[29a] Hindermann and Geigy, USP 2,472,109.

[29b] Ciba, SP 233,083–4.

[28] See p. 618.

producing substantivity for cotton is illustrated by the bis-pyrazolone prepared from the urea (XI) of diaminostilbenedisulfonic acid, through the usual stages of the bis-hydrazine condensed with acetoacetic ester.[30]



(XI)

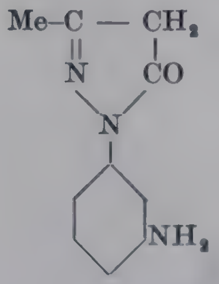
Coupling the bis-pyrazolone with two moles of diazotized anthranilic acid (or its derivatives), the disazo dyes can be converted into copper complexes, which are fast yellow direct cotton dyes.[31] A green direct cotton dye is obtained by condensing 4-acetamido-4′-hydrazinodiphenyl (from monoacetylbenzidine) with acetoacetic ester, coupling the pyrazolone with diazotized 4-chlorometanilic acid, hydrolyzing the acetyl group, diazotizing and coupling with the monoazo dye (2,5-dichloroaniline $\xrightarrow{\text{acid}}$ H-acid).[31a]

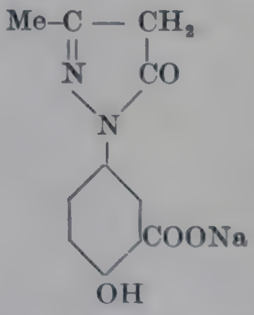
MISCELLANEOUS PYRAZOLONE DERIVATIVES

1-*m* (or *p*)-Aminophenyl-5-pyrazolones. Azo dyes derived from 1-aminophenyl-5-pyrazolones (e.g., XII) lend themselves readily to diazotization and development on the fiber, while azo dyes in which the amino and azo groups are attached to the same benzene or naphthalene ring are sometimes difficult to diazotize and the diazonium salts are sluggish couplers. Azo dyes (A $\longrightarrow$ XII or its *p*-amino isomer) are also useful for phosgenation (cf. Benzo Fast Copper Red RL) and cyanuration. The 1-aminophenylpyrazolones can be phosgenated first and then coupled with diazonium salts.[32] 1-(4′-Cinnamoylamido-4-biphenylyl)-5-pyrazolone-3-carboxylic acid gives dyes substantive to cotton.[33]

The dye (benzidine-3,3′-disulfonic acid $\rightrightarrows$ two moles XII), when tetrazotized on the fiber and developed with (I), gives fast yellow shades.[34] Pyrazolones containing an aminophenyl group in the 1-position are also useful for the preparation of disazo and polykisazo dyes in substance. As mentioned earlier, pyrazolones with a salicylic acid residue in the 1-position

(XII)





(XIII)

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[30] Ciba, BP 503,609.
[31] BP 580,174.
[31a] Ciba, SP 223,703.
[32] Ciba, SP 220,411–4.
[33] Ciba, SP 220,106–10.
[34] Murphy, Rossander and du Pont, USP 2,191,801.

are useful intermediates for the preparation of metal complexes in substance or of acid and direct cotton dyes, which may be metallized on the fiber. An example[35] of a trisazo dye in which two such pyrazolone intermediates are employed is (salicylic acid $\xleftarrow{1}$ 3-hydroxybenzidine $\xrightarrow{2}$ XII $\xrightarrow{3}$ XIII). In tetrazotized 3-hydroxybenzidine, the *o*-hydroxydiazonium group is weaker coupling; the other is therefore first coupled with the slow-coupling salicylic acid, and at the second stage the *o*-hydroxydiazonium group is coupled with the pyrazolone molecule. 4-Amino-5-pyrazolone can be diazotized and coupled with acetoacetanilides and with *o*-coupling components, and the azo dyes then metallized.[36] 3-Amino-5-pyrazolones can be coupled with diazonium salts and metallized.[37]

The methylene group in the pyrazolones, as in indoxyl, condenses with aldehydes, nitroso and similar compounds and forms a series of colored substances; with ferric chloride oxidation to pyrazole blue takes place.[38] Aminoantipyrine also gives rise to deeply colored derivatives.[39] These products have no technical value.

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[35] Ciba, BP 580,486; see also Ciba, BP 578,964.

[36] Nies and American Cyanamid, USP 2,446,662; 2,447,867.

[37] Long, Lewis and American Cyanamid, USP 2,437,645.

[38] Knorr, *Ann.* **238**, 137 (1887); A. E. and B. A. Poraîkoshits and Ginsburg, *J. Gen. Chem.* (*U.S.S.R.*) **17**, 1752 (1947).

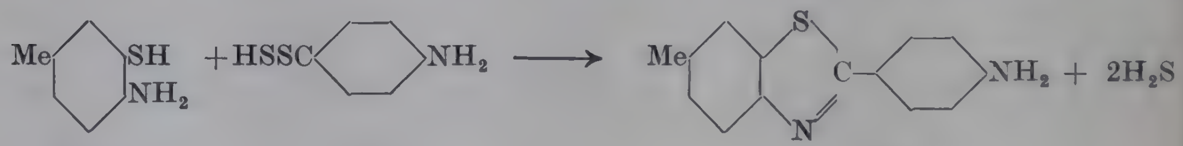
[39] Emerson and Beegle, *J. Org. Chem.* **8**, 433 (1943).

Chapter XIX

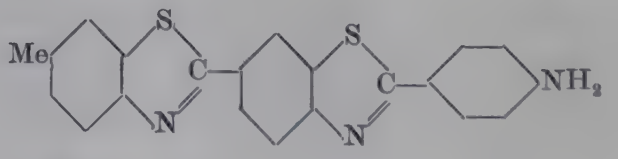
THIAZOLES

The thiazole ring is present in some members of several classes of dyes, such as the direct cotton colors, sulfurized vat dyes and the cyanine dyes; but the thiazole dyes are very limited in number and there are only a few representatives in each class.[1-6] The thiazole ring is favourable to substantivity for cellulose. In the azo series the thiazoles constitute a very small group, with dehydrothiotoluidine as the common intermediate.

When *p*-toluidine (one mole) is heated with rather more than two atoms of sulfur, the temperature being raised from 180 to 230° in the course of several hours and maintained at 230° until the evolution of hydrogen sulfide ceases (about 20 hours), the product is a mixture of dehydrothio-*p*-toluidine (I) and Primuline Base (II). They are separated technically by vacuum distillation or in the laboratory with boiling alcohol in which dehydrothiotoluidine is more soluble.[7] Dehydrothiotoluidine comes off at 230–240°/2–3 mm. The relative proportions of (I) and (II) depend on the proportion of sulfur; for the manufacture of (I) the ratio of sulfur to *p*-toluidine is 4:10, and for (II) it is 7:10. The mechanism of the reaction probably consists in the formation of the thiophenol (III) and the dithiobenzoic acid (IV), which then condense to form dehydrothiotoluidine (I). The interaction of (I) with a further molecule of (IV) then leads to Primuline Base (II). By prolonging the action, it is possible to introduce a third



(III) (IV) (I)



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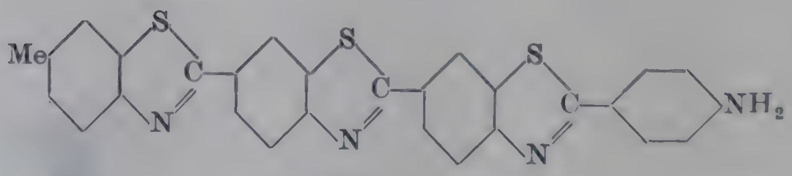
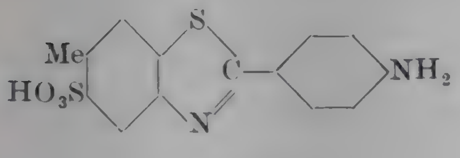


(V)

[1-6] As in Chapter XII.

[7] *BIOS* 986.

thiazole ring, and Primuline in fact usually contains a small amount of (V).[8] On cooling, the reaction mixture is powdered and sulfonated with about five times its weight of 20–25% oleum at a temperature not exceeding 40°, until a sample dissolves in aqueous ammonia. The mixture is blown into water, the orange-yellow precipitate filtered, and treated with concentrated ammonia; Primuline sulfonic acid dissolves as the ammonium salt, while dehydrothiotoluidine sulfonic acid forms a sparingly soluble ammonium salt, which is separated by filtration. The sodium salt of Primuline sulfonic acid is finally salted out from the filtrate. Bogert and Snell[9] have shown that both in dehydrothiotoluidinesulfonic acid (VI) and in Primuline the sulfonic group enters the *o*-position to the methyl group in the benzothiazole ring, and not the *o*-position to the amino group in the 2-phenyl ring as believed for many years.



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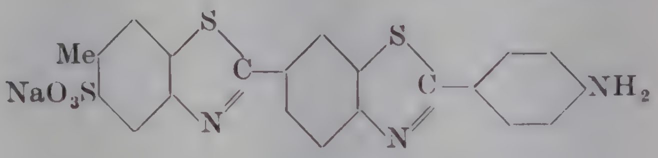

Primuline

Primuline (Green, 1887; CI 812) dyes cotton directly a greenish yellow, which is too fugitive to be of practical value. If the amino group is diazotized on the fiber and developed with resorcinol (orange), β-naphthol (red), R-salt (maroon), *m*-phenylenediamine (brown), etc., a range of orange, red and brown shades, much faster to washing, is obtained. Primuline was the first " ingrain color " in the sense that it was a dye with marked affinity for cotton, and a series of dyes of different shades and with improved fastness could be produced by a process of diazotization and development on the fiber. This is valuable as an aftertreatment process for direct cotton dyes, although Primuline itself has largely lost its importance.

The sensitivity of diazotized Primuline to light has been used for producing colored photographic prints on cotton fabrics and on paper. The dyed material is treated with nitrous acid and dried in the dark. On exposing to light behind a positive and developing with alkaline β-naphthol or other coupling component, a colored positive is produced by the decomposition of the diazonium salt in the portions exposed to light. Such " diazo " or " diazotype " processes are now extensively used for colored productions of machine drawings, printed and typed matter, replacing blue prints which are much more tedious to produce (see Chapter IV).

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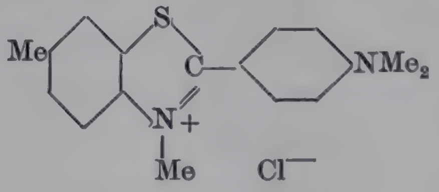
[8] Cf. Fierz-David and Brunner, *Helv. Chim. Acta* **27**, 1 (1944). See also Geigy, SP 239,006.

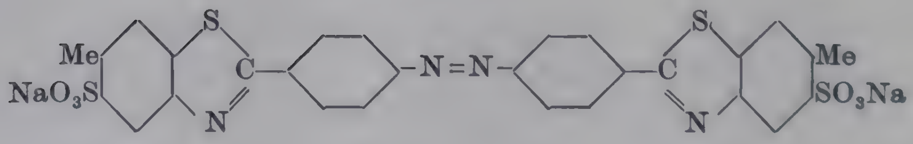
[9] Bogert and Snell, *Color Trade J.* **14**, 109 (1924).

Dehydrothiotoluidine and its sulfonic acid have no dyeing properties, but they are useful intermediates. A basic dye, prepared from the base by heating it with methanol and hydrochloric acid at about 170° in an autoclave for a few hours, is Thioflavine T (Green and Lawson, 1888) (C; CI 815). In the course of a synthesis of substituted benzothiazoles, the constitution of Thioflavine T has been confirmed.[10] As a basic color, it dyes wool and silk directly, and cotton on a tannin mordant, a greenish-yellow. At the present time its use is mainly in calico printing, both in direct and discharge styles. Thioflavine S (Rosenheck, 1888) (C; CI 816) is prepared by methylation and sulfonation of Primuline Base; the two reactions can also be carried out in the reverse order.[11] Unlike Primuline, Thioflavine S is no longer diazotizable, and it is used as a direct cotton dye for canary-yellow shades where the fastness requirements are low.

Oxidation of the sodium salt of dehydrothiotoluidine sulfonic acid (VI) with sodium hypochlorite at 70–80° yields the important azo dye Chlorophenine (Green, 1887; CAC, CI 814) (Chloramine Yellow, By) (Direct Fast Yellow). Its constitution[12] as an azo dye, and not a stilbene derivative, has been proved by its synthesis by the route: *m*-mercapto-*p*-toluidine$\longrightarrow$ 2-*p*-nitrophenyl-6-methylbenzothiazole$\xrightarrow{\text{reduce}}$azo compound $\xrightarrow{\text{disulfonate}}$ Chlorophenine. It is used for dyeing cream and yellow shades on cotton, wool and silk because of its excellent leveling properties and fastness to light, notwithstanding its poor fastness to washing.[13] Oxidation of dehydrothiotoluidine-5,7-disulfonic acid in caustic soda solution with hypochlorite, first at 35° and subsequently at 70°, gives Sirius Supra Yellow RR (IG) which has a light fastness of 6–7.[14, 15] Similar oxidation of Primuline in



Thioflavine T



Chlorophenine

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[10] Bogert and Taylor, *Coll. Czech. Chem. Comm.* **3**, 480 (1931).

[11] According to Fierz-David, Thioflavine S is obtained by sulfonation of Thioflavine T.

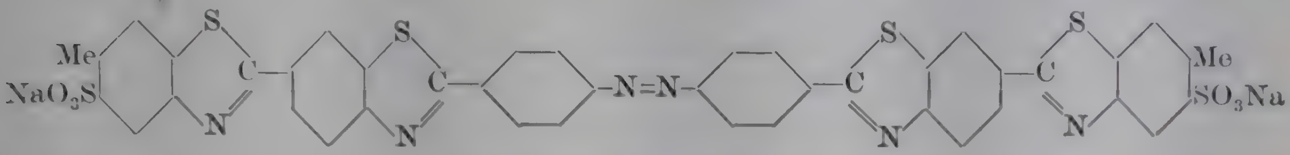
[12] Bogert and Bergeim, *Proc. Natl. Acad. Sci.* U.S. **10**, 318 (1924).

[13] Basic dyes of this type, claimed to have excellent fastness to washing, have been mentioned in Chapter XII.

[14] *BIOS* **1482.**

[15] The characterization of Sirius Supra Yellow RR (Naphthamine Yellow NN), (VI) and Primuline is discussed by Schubert, *Ann.* **558,** 10 (1947).

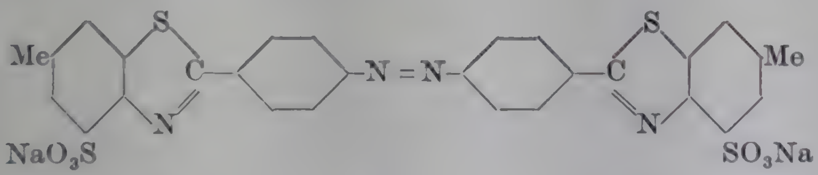
alkaline solution with chlorine at about 0–5° gives Sirius Supra Yellow RT, a useful yellow direct cotton dye characterized, like other Sirius and Sirius Supra dyes, by high light fastness.[14]



Sirius Supra Yellow RT

Fierz-David and Brunner[8] have shown that in the oxidation of dehydrothiotoluidine sulfonic acid with sodium hypochlorite the azoxy compound is first formed quantitatively, which then reacts with more hypochlorite to form the azo dye and sodium chlorate. It is preferable, however, to reduce the azoxy compound with sodium sulfide, sulfite or glucose (but not sodium hydrosulfite which will reduce the azo compound further to the hydrazo compound). The azo group in Chlorophenine (and in Sirius Supra Yellow RT) cannot be reduced beyond the hydrazo stage, so that in calico printing a white discharge cannot be obtained.

By the oxidation of dehydrothiotoluidine to the azoxy compound and reduction with sodium sulfide, Fierz-David and Brunner[8] prepared the unsulfonated analog of Chlorophenine. Sulfonation gave an isomer of Chlorophenine, considered to be (VII), which dyed a purer shade of yellow



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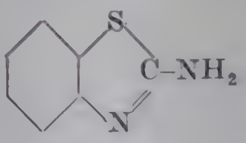

(VIII)

than Chlorophenine; the fastness to light was 7–8 compared to 6 for Chlorophenine.

Bogert and Allen[16] have prepared five isomers of dehydrothio-*p*-toluidine, carrying the methyl and amino groups in other positions, and have converted them into dyes analogous to Thioflavine T. They have also prepared 2-(*p*-aminophenyl)-5- and 7-methylbenzothiazole, and have converted them by sulfonation and hypochlorite oxidation into isomers of Chloramine Yellow, scarcely distinguishable from it in tinctorial properties.[17]

When 2-aminobenzothiazole (VIII) is treated with hypochlorite, a bright red color develops immediately and the essential product of the reaction is the azo compound. Paper impregnated with (VIII) or one of its *C*-substituted derivatives will develop a deeply colored blot as soon as an ink eradicator, such as hypochlorite solution, is applied; and (VIII) has therefore been found useful in the preparation of paper, legal documents and cheques to be protected against forgery.[18]

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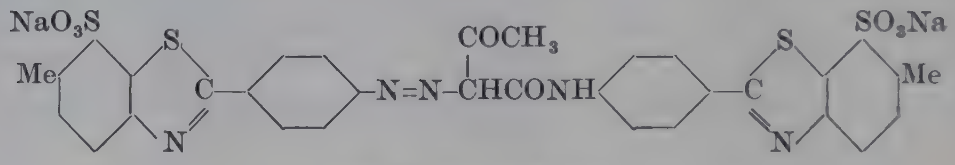
[14] See p. 624.

[16] *JACS* **49,** 1315 (1927).

[8] See p. 623.

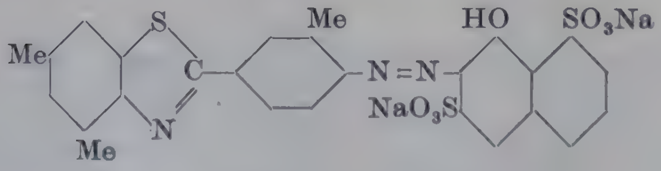
[17] *Ind. Eng. Chem.* **18,** 532 (1926).

Dehydrothiotoluidine sulfonic acid (VI), its *m*-xylidine analog (IX), and Primuline have been used as diazonium components for the preparation of direct cotton dyes. Dianil Yellow R (Scholl, 1899) (MLB; CI 649) is a useful yellow dye prepared by coupling diazotized Primuline with phenylmethylpyrazolone. Among other dyes prepared from (VI) or Primuline may be mentioned: Dianil Yellow 3G (MLB; CI 647) (Primuline → acetoacetanilide); Dianil Yellow RR and RRL (mixtures of VI and Primuline → 4′-sulfophenylmethylpyrazolone); Dianil Yellow 5G (VI + I–7–SO$_3$Na → acetoacetanilide); Zambesi Orange R (IG) (VI → *m*-nitrophenylmethylpyrazolone; reduce the nitro group); Dianil Orange G (Primuline → 1-*p*-sulfophenyl-5-pyrazolone-3-carboxylic acid).[4] In spite of their poor fastness to light, these dyes, which have good fastness to alkali, are used in the paper and textile industries. Dianil Yellow 3GW is an IG dye not yet offered for sale, which is prepared by coupling diazotized dehydrothiotoluidine-7-sulfonic acid with the acetoacetylide of the same amine.[3, 19]

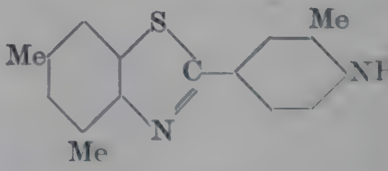


Dianil Yellow 3GW

The dye has very good affinity for cotton and good fastness to washing and alkali, considering it is a direct cotton dye, but the fastness to light is unsatisfactory (3). Suitable second components in the naphthalene series are ε-acid, γ-acid, and 1-chloro-8-naphthol-3,6-disulfonic acid, the shades



Erika B extra



(IX)

produced being rose to pink. Examples are Erika 2GN (Schultz, 1888) (AGFA; CI 126) (I → ε-acid), Erika B extra (AGFA; CI 130), Diamine Rose BD (Weinberg, 1893) (C; CI 128) and Chloramine Violet FFB (IX → acetyl-H-acid). These dyes have very low light fastness (1), but they level well, and being dischargeable by hydrosulfite and by chlorate, they are also useful in printing. Rosophenine 10B (Green, 1893) (CAC; CI 225) (VI⟶NW-acid) dyes cotton pink to crimson, and is also applicable to wool. A dye in this series with good fastness to light is Sirius Scarlet B (dehydrothiotoluidine disulfonic acid⟶X).[6]

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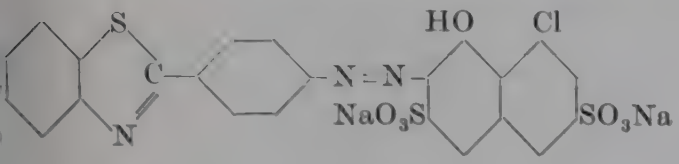
[18] Kirk, Johnson and Blomquist, *J. Org. Chem.* **8**, 557 (1943).

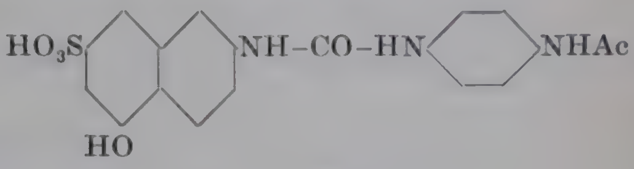
[4] See p. 622.

[3] See p. 622.

[19] See also Ciba, SP 217,489.



Diamine Rose BD



(X)

Alphanol Brown B (C) (Mixture of Primuline and VI⟶phenyl-γ-acid) is a useful acid color for wool;[2] it has good fastness to wet treatments (3–4), but the fastness to light is only 3.

By condensing diazotized (VI) with (VI) in faintly alkaline solution, the diazoamino compound (Ar–N=N–NH–Ar), Clayton Yellow (CAC; CI 813) (Thiazole Yellow G, By), has a limited use as a bright yellow direct cotton dye, although it has very poor fastness to light (1–2) and to alkali; it has more interest as an indicator for caustic alkali (yellow to red).

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[6] See p. 622.

[2] See p. 622.

CHAPTER XX

STILBENE DYES

Stilbene dyes are classified separately, but as a sub-division of the azo dyes, since they are prepared by a distinctive method starting from a common intermediate, and they contain one or more azo groups.[1–6]

DYES FROM *p*-NITROTOLUENE-*o*-SULFONIC ACID

Yellow to orange dyes of good fastness and substantivity for cotton are prepared by boiling *p*-nitrotoluene-*o*-sulfonic acid (I) with dilute caustic soda solution, and oxidizing or reducing the products. The stilbene azo dyes form a numerous group, but all are derived from (I) as the common intermediate. A few disazo dyes are prepared from tetrazotized 4,4′-diaminostilbene-2,2′-disulfonic acid, and the great majority of the stilbene dyes are prepared from (I) by characteristic reactions in which diazotization and coupling are not involved. Because of the ease with which (I) and its derivatives lend themselves to condensations leading to dyes with excellent dyeing properties, marked especially by fastness to light, there has been continued interest in the series, of which the first member was made by Walter in 1883, and many stilbene colors are to be found in the modern commercial range of azo dyes. They are mostly dyes of undetermined constitution; the general nature of the reactions and the constitution of some of the dyes were elucidated by the early researches of Green, and little progress has since been made on the constitutional side.

When (I) is heated with caustic soda solution, dyes can be directly prepared by suitable adjustment of the alkali concentration, temperature and time of reaction. The first stage of the self-condensation is 4,4′-dinitrosostilbenedisulfonic acid (II), which yields the diamine (III) by reduction with iron and acid. When the diamine is tetrazotized and coupled with phenol, the product, Brilliant Yellow (Bender, 1886) (CI 364), is too sensitive to alkali to be useful as a dye, and it is used as an indicator. Ethylation of the hydroxyl groups gives Chrysophenine G (Bender, 1886) (L; CI 365), a largely used yellow direct cotton dye with good fastness to light (4–5) and alkali, valuable also for dyeing wool and other fibers. Diphenyl Chrysoine G (Gy; CI 631) would appear to be identical with Chrysophenine. By coupling tetrazotized (III) with two moles of salicylic

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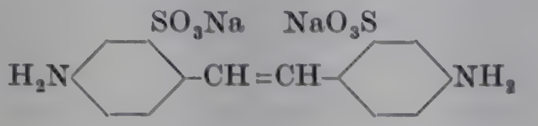
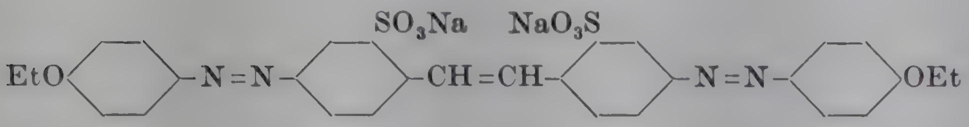
[1–6] As in Chapter XII.

acid (Hessian Yellow, By; CI 366), α- or β-naphthylamine, Brönner acid and other components, a series of dyes for cotton and wool are obtained,

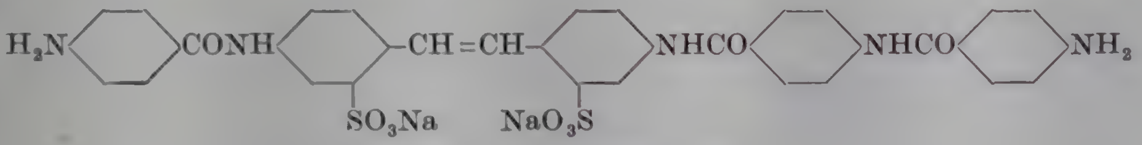


(III)



Chrysophenine G

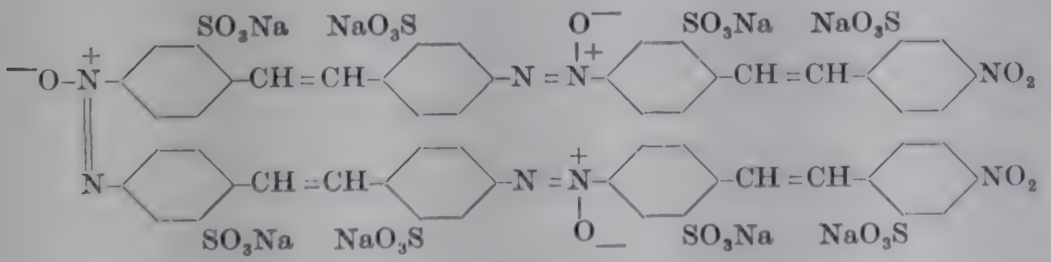
which are obsolete as commercial dyes. Diazo Fast Yellow 2G (IG), prepared by condensing (III) with one mole of *p*-nitrobenzoyl chloride and one of *p*-(*p*′-nitro) benzamidobenzoyl chloride, and reducing with iron and acid,[7,8] has affinity for cotton, and a yellow shade with light fastness 4 is



Diazo Fast Yellow 2G

produced by tetrazotizing on the fiber and developing with phenylmethylpyrazolone.

Heating (I) with aqueous caustic soda under specific conditions, the main tinctorial constituent of the product is Sun Yellow (Walter, 1883) (Gy; CI 620) (Curcumine S), which is still employed commercially for golden yellow shades on cotton, wool and silk; it is usually formulated as an azo-azoxy-bis-stilbene derivative. By adding a reducing agent, such as sodium sulfite, glucose, and others suggested in patents, to the reaction mixture of (I) and alkali, orange dyes (Mikado Orange) (Bender, 1885) (L; CI 621) (Diamine Orange D; C) are obtained, which consist essentially



Curcumine S

of a product usually formulated as a disazo-bis-stilbene. As direct cotton colors, they are useful for orange to brown shades. The closed cyclic

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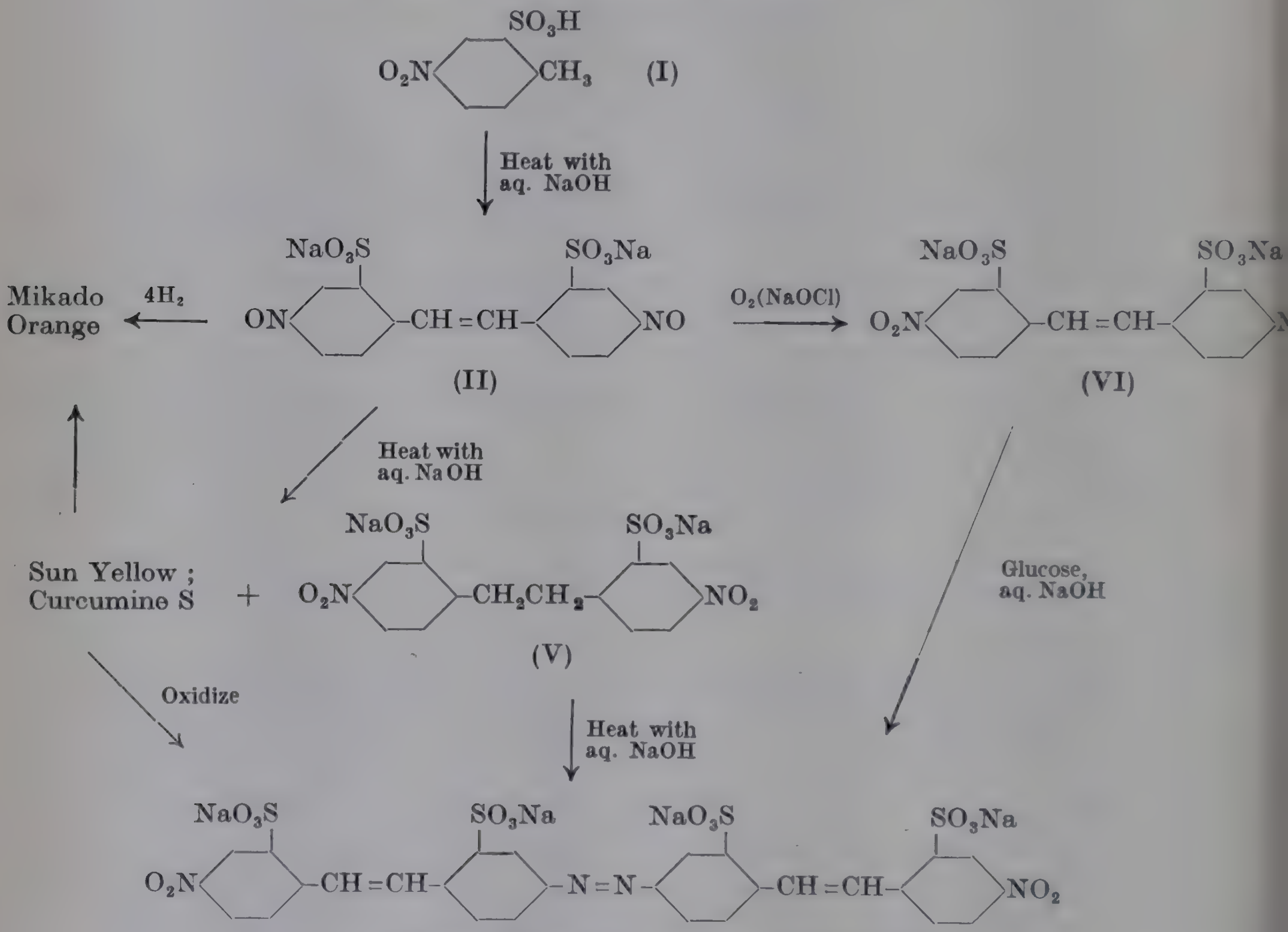
[7] *FIAT* **1313,** III.

[8] CI 654 assigns to Diazo Fast Yellow 2G (By) the structure of a urea derivative identical with Diazo Light Yellow 2G.

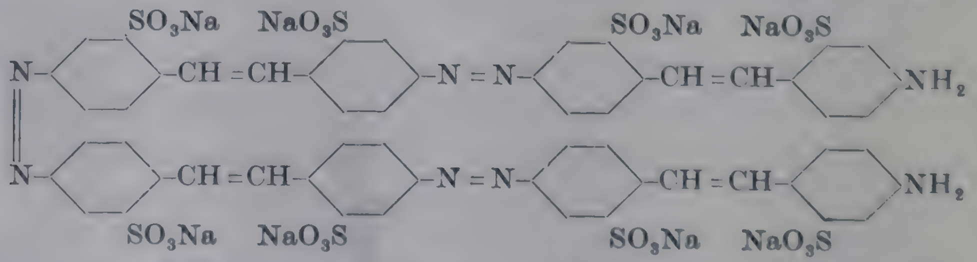
structures[9] ascribed to Sun Yellow and Mikado Orange are stereochemically impossible, and the dyes are probably linear, polymeric condensation products. IG have proposed the indicated structure for Curcumine S; and they consider Diamine Orange D to be a mixture of Curcumine S (as the major constituent) and its reduction product (IV). By acetylating a brand of Diamine Orange D which was mainly (IV) a valuable bright dye (Diamine Orange GR) was obtained.[10]

CHART 1

DYES FROM *p*-NITROTOLUENE-*o*-SULFONIC ACID


(I)
Heat with aq. NaOH
Mikado Orange
4H₂
(II)
O₂(NaOCl)
(VI)
Heat with aq. NaOH
Sun Yellow ; Curcumine S
+
(V)
Glucose, aq. NaOH
Oxidize
Heat with aq. NaOH

Mikado Yellow G ; Stilbene Yellow 8G



(IV)

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[9] Green and Crosland, *JCS* **89**, 1611 (1906).

[10] *BIOS* document quoted in *Annual Repts. Soc. Chem. Ind. London* **32**, 60 (1947).

A by-product in the preparation of Sun Yellow is the disodium salt of dinitrodibenzyldisulfonic acid (V). By oxidizing Curcumine S with nitric acid (Bender, 1886), hypochlorite or chromic acid, or heating (V) further with alkali (Green and Wahl, 1897) or by the glucose-alkali reduction of the disodium salt of dinitrostilbenedisulfonic acid (VI), which is obtainable by the oxidation of the dinitroso compound (II), another useful yellow dye, Mikado Yellow G (L; CI 622) (Stilbene Yellow 8G; CAC), is prepared. Treatment of dinitrostilbenedisulfonic acid with caustic soda solution and formaldehyde at 90–93° gives Stilbene Yellow 3GX (IG), a dye with good light fastness (4–5).[2]

Diamine Orange GR, released by the IG in 1943, is a brilliant dye for cotton and viscose with good light fastness. It is prepared by treating (I) with aqueous caustic soda solution at 85° to form nitro derivatives of azo- and azoxystilbenes, reducing the nitro groups with sodium sulfide, and acetylating the amino groups.[3]

The condensation of one mole of (III) with two moles of cyanuric chloride gives an intermediate useful for the preparation of greenish yellow, orange and red-brown dyes; such dyes have good fastness to light, particularly if they can be aftertreated on the fiber with copper sulfate.[11] The polyazo dyes (III $\rightrightarrows$ anthranilic acid, 2 moles $\rightrightarrows$ phenylmethylpyrazolone, 2 moles) give red aftercoppered shades.[12]

DYES FROM THE CONDENSATION OF AMINES WITH (I), (V) AND (VI)

4,4′-Dinitrostilbene-2,2′-disulfonic acid (VI) is an important intermediate. It can be prepared in 80–90% yield by heating (I) with 3% caustic soda solution (20 parts) to 50–55°, and gradually adding 5% sodium hypochlorite solution containing 5% caustic soda until a slight excess of chlorine remains; after agitating for a few hours at 50–55°, (VI) is salted out. While the dyes so far described are self-condensation products of (I), a wide range of useful dyes becomes available by condensing primary amines (e.g., aniline, *p*-phenylenediamine, benzidine, aminoazobenzene) with (VI), (I) or the dibenzyl derivative (V). When (I) is used for such condensations it is probable that the dinitrosostilbene (II) is first formed, which then condenses with primary amines to form azo dyes. The reaction is of interest as a method of preparing azo dyes which does not involve diazonium coupling.[13] The products are mixtures of dyes, but by the standardization of conditions a reproducible mixture with specific dyeing properties can be obtained.

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[2] See p. 628.

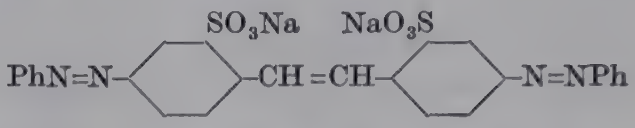
[3] See p. 628.

[11] Ciba, BP 578,014; 595,181; USP 2,399,066; 2,399,447; 2,421,553; 2,459,435; SP 242,159. See also Geigy, SP 239,758; 244,250–62; BP 630,181; Ciba, SP 233,845; 245,576.

[12] Ciba BP 592,614; USP 2,405,353.

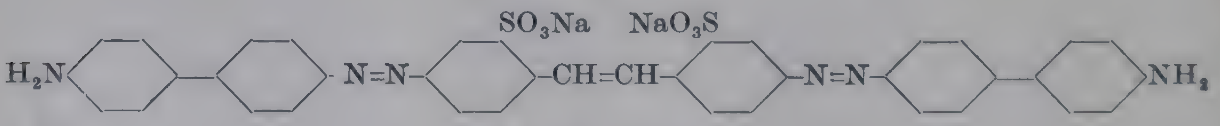
[13] IG, BP 451,673; see also Geigy, SP 243,962–5.

Thus, by the interaction of (VI), aniline and sodium hydroxide, followed by oxidation with hypochlorite, a mixture of Stilbene Yellow 8G and disodium 4,4′-bisbenzeneazostilbene-2,2′-disulfonate (VII) is produced


(VII)

(Diphenyl Citronine G; Gy) (Ris, 1897; CI 624) which is a greenish yellow direct cotton color with good fastness properties. Condensing (I) with *p*-phenylenediamine and caustic soda under carefully controlled conditions, the main product Direct Brown R (Ris, 1890) (Gy; CI 625) is the *p,p*′-diamino derivative of (VII), which dyes cotton an orange-brown of moderate fastness; the free amino groups can be diazotized on the fiber and developed (with β-naphthol, bordeaux; with α-naphthylamine, black). The same reaction under different conditions gives a reddish orange dye (Diphenyl Orange RR) (Gy; CI 626), which is also capable of diazotization and development on the fiber. Sirius Supra Orange 5G (IG) is prepared by heating (I) with aqueous caustic soda at 27–63° during several hours, and then with 4-aminoazobenzene-4′-sulfonic acid at 103–104° for 12 hours in an autoclave.[2] Diphenyl Chrysoine G is prepared by heating (I) with *p*-aminophenol and aqueous caustic soda and ethylating the product.

Stilbene dyes with diazotizable amino groups find further use as first components for the preparation of polyazo dyes in substance. Diphenyl Fast Brown (Ris, 1899) (Gy; CI 629) is such a dye, probably containing four azo groups, prepared by diazotizing Diphenyl Orange RR and coupling with phenyl-γ-acid. A dye (Chicago Orange 3G) (Ris, 1892) (Gy; CI 633), which may more definitely be formulated as a tetrakisazo dye, is prepared by tetrazotizing Chicago Orange G (Gy; CI 633) and coupling with two moles of salicylic acid. Chicago Orange G is an analog of Diphenyl Citronine G and Direct Brown R, prepared by condensing (I) with benzidine in presence of caustic soda.


Chicago Orange G

A series of bright orange dyes of the Sirius Supra range (IG), which have high light fastness (6–7), excellent fastness to alkali (5), and moderate fastness to acid (3), are obtained[2, 3] by condensing dinitrostilbenedisulfonic acid (VI) with aminoazo compounds in presence of aqueous caustic soda; in some cases the product, without isolation, is reduced with glucose or sodium sulfide.[2] By condensing (VI) with the monoazo dye (sulfanilic acid→cresidine), Sirius Supra Orange 3R is obtained; the monoazo dye (*p*-anisidine-2-sulfonic acid→*p*-xylidine) gives Sirius Supra Orange RRL; the monoazo dye (sulfanilic acid→*m*-toluidine) gives the 7G brand; Benzo Fast Chrome Orange R (IG) is prepared by the condensation of (VI) with the monoazo dye (VIII).[3] Benzo Fast Chrome Red G, issued by IG in 1940, is similarly constituted, cresidine being used in place of *p*-xylidine in (VIII); the dye has better light and wet fastness than the older chrome-developed dyes for cotton and it is useful for dyeing wool-cellulose union fabrics since it is fast to cross-dyeing wool with chrome dyes. Condensation of (VI) with the dye (*p*-anisidine-2-sulfonic acid→cresidine) gives Sirius Supra Scarlet GG. Typical conditions[2] for these condensations are to mix (VI) (one mole) with an equal weight of water, caustic soda (one mole as a 40% solution) and the aminoazo compound (e.g., sulfanilic acid→*m*-toluidine for Sirius Supra Orange 7G) (1.75 moles). After agitating overnight, the paste is transferred to an autoclave, together with caustic soda (3.5 moles) and water to make up a caustic soda concentration of about 3.6%. The mixture is then heated at 102–103° for 2–3 hours. The dyestuff is precipitated by salting out and neutralizing excess alkali with hydrochloric acid.

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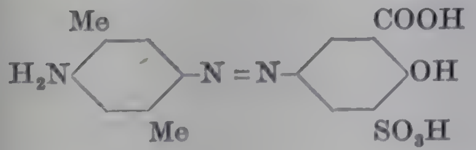
[2] See p. 628.

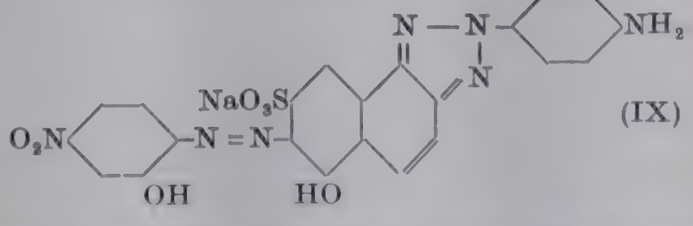
[3] See p. 628.

By condensing 4-aminoazobenzene-4′-carboxylic acid with (VI) and reducing with glucose the product is Sirius Supra Orange GR; 4-aminoazobenzene-4′-sulfonic acid gives the GGL or 7GL brand according as the proportion of the azobenzene derivative is 1.15 or 1, and the reducing agent is sodium sulfide or glucose.

A series of useful brown dyes for cotton are obtained by condensing (VI) with *p*-aminoazo compounds, the reaction being carried out by heating them with 0.5 to 1% aqueous caustic soda at 100–103° in an autoclave for several hours.[2] Thus, condensation of (VI) with the monoazo dye (sulfanilic acid →α-naphthylamine) in the proportion of 1:0.62 gives Diamine Fast Brown G (IG), which has a light fastness of 5–6 as well as very good fastness to acid and alkali (4–5); when the proportion of the monoazo dye is increased to 1.09, the product is Sirius Supra Brown 3R, which has very good fastness to acid and alkali (4–5) and light (6). Sirius Supra Brown R, which is similar in its fastness properties to the 3R brand and is less reddish in tone, is



(VIII)



(IX)

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[2] See p. 628.

[3] See p. 628.

prepared by condensing (VI) with the monoazo dye (sulfanilic acid——→ cresidine) in equimolecular proportion, and reducing the product with sodium sulfide. Condensation of (VI) with (2-naphthylamine-3,6-disulfonic acid——→α-naphthylamine) gives Diamine Fast Brown GB (IG), which has only moderate light fastness (3–4).

Fast bright dyes (e.g., Diphenyl Fast Yellow, Gy; Ris, 1897; CI 632) with a high affinity for both cellulosic and protein fibers are obtained by condensing (I) or (V) or (VI) with dehydrothiotoluidine sulfonic acid or Primuline. When (I) or 4,4′-dinitrostilbene or (V) is condensed with monomethylaniline, yellow crystalline products are obtained.[14] Orange to deep brown shades of exceptional fastness to light, chlorine and washing are obtained by aftertreating on the fiber with copper sulfate or chromium fluoride the azo dyes obtained from the condensation of 5-aminosalicylic acid, or an azosalicylic acid containing a free amino group, with (I), (V) or (VI).[15] Stilbeneazo dyes, claimed to be homogeneous and to have very good discharge properties as well as good light fastness, have been obtained by IG by stepwise condensation in alkaline solution of 4,4′-dinitrostilbene-2,2′-disulfonic acid with *p*-phenylenediamines (1 or 2 moles at 50° or 80–85° respectively) to give monoamino or diamino compounds. These can be diazotized or tetrazotized and coupled with a *p*-coupling phenol, the product being alkylated to inhibit alkali sensitivity.[16] The orange dye obtained by condensing (VI) with the monoazo dye (amido-G-acid——→aniline) is stated to be remarkably fast to chlorine, light and washing.[17]

Among the complex amines suggested for condensation with (VI) are naphthatriazoles, such as (IX); since the yellow-brown dye has an *o,o′*-dihydroxyazo group, it can be converted into a copper complex in substance or on the fiber.[18] Improved fastness to washing is claimed for the yellow, orange, brown and olive dyes obtained by condensing (I) in alkaline medium with amino-diaryltriazoles containing at least one carboxyl or sulfonic group; the dyes may be metallized.[19]

DYES FROM 4-NITRO-4′-AMINOSTILBENE-2,2′-DISULFONIC ACID

4-Nitro-4′-aminostilbene-2,2′-disulfonic acid (X) is an important stilbene intermediate from which direct cotton dyes with high light fastness can be prepared.[2] Coupling diazotized (X) with phenol and then methylating, the product is Sirius Orange I. Reduction of Sirius Orange I with glucose gives

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[14] Sandoz, BP 586,411.

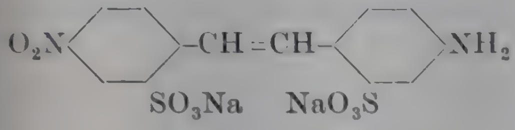
[15] Cassella, DRP 422,466; see also Ciba, SP 217,235; and Geigy, SP 228,817–24. For other types of metallizable aminoazo compounds with which (VI) may be condensed, see Geigy, BP 532,970; 555,867.

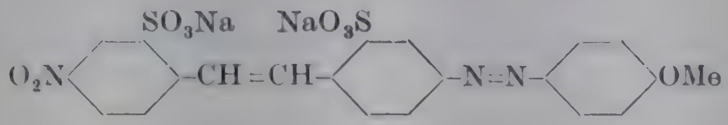
[16] SP 225,559; 230,635–6; 232,606; 236,691–2.

[17] Allied Chemical and Dyestuff, USP 2,386,847.

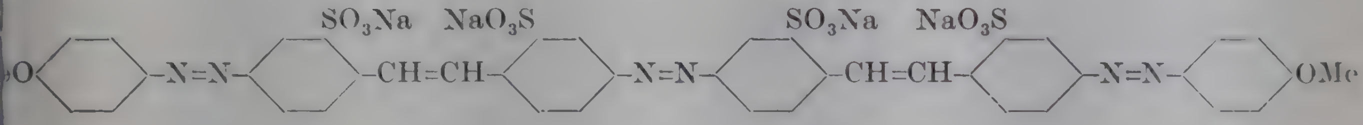
[18] Geigy, BP 542,731. See also SP 231,890.

[19] Geigy, BP 556,580; see also Knight and ICI, BP 590,426. According to Knight, *J. Soc. Dyers Colourists* **66**, 410 (1950), Solophenyl Brown RL and Solophenyl Gray GL (Gy) are probably coppered dyes of the stilbene-azo class.


(X)


Sirius Orange I

the trisazo dye, Sirius Supra Orange F3G, which has light fastness 6–7.


Sirius Supra Orange F3G

Copper complexes of azo dyes derived from (X) have been described in Chapter XIII.

By converting (X) into a pyrazolone, reducing the nitro group and phosgenating, the product is useful for the preparation of disazo dyes with good fastness after coppering on the fiber.[20] Several patents deal with dyes from (X) which may be aftercoppered on the fiber or converted into copper complexes in substance[21] and with cyanuric chloride condensation products in which (X) is one of the reactants. Thus a fast-to-light orange dye is obtained by condensing cyanuric chloride with one mole of (X) and two moles of 5-aminosalicylic acid and reducing the product to an azo or azoxy compound by means of glucose and alkali.[22] Another route for azo dyes from (X) is to convert it to a triazole by diazotizing, coupling with a component such as 2-naphthylamine-6-sulfonic acid, and oxidizing in the known manner; the triazole is then used for subsequent reactions, e.g., condensation with the copper complex of an aminoazo dye.[23]

THE BLANKOPHORS

Colorless stilbene derivatives with affinity for cellulose fibers and the property of fluorescing in ultraviolet light and daylight have been marketed as whitening agents for use on laundried or bleached textiles and paper. They are also recommended for improving the whites in discharge printing. The bis-*N*-benzoyl derivative of diaminostilbenedisulfonic acid (III) appears to be the first substance suggested for such "fluorescence bleaching."[24] Blankophor R (IG) is prepared by the interaction of the sodium salt (III) with phenyl isocyanate in aqueous solution. Blankophor B, which has greater substantivity for cellulose and better wash-fastness, is (XI) prepared by condensing one mole of (III) with two moles of the product of the condensation of one mole of cyanuric chloride with one of aniline.[25] A mixture of Blankophor R and Anthralan Green GB (2.5%) is marketed as Blankophor RG for the production of a slightly greenish shade of white.

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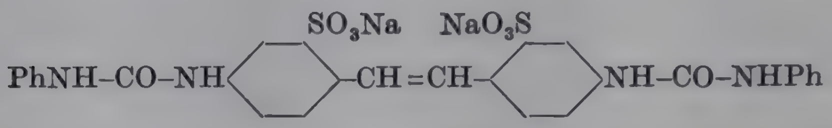
[2] See p. 628.

[20] Ciba, BP 580,174; see also SP 220,215; 220,750–1; 222,139-48; 225,560; 246,424–7.

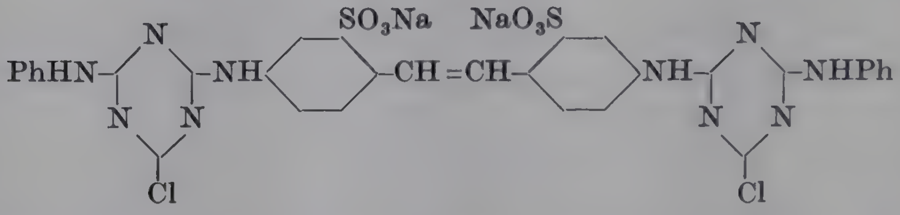
[21] Geigy, BP 591,354; SP 238,444–50; USP 2,468,204.

[22] Geigy, USP 2,368,844; SP 240,115–26. See also SP 236,586; BP 616,523; Ciba, SP 228,825–30.

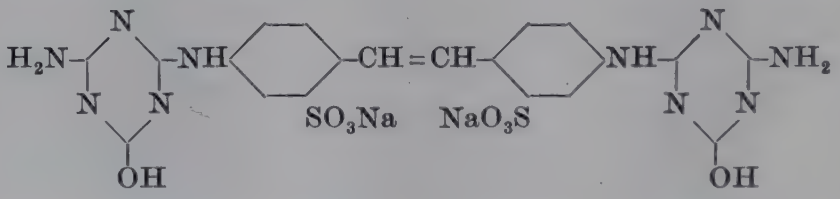
[23] Geigy, USP 2,462,405; SP 229,350–5.



Blankophor R



(XI)



(XII)

The condensation product of (XII) with formaldehyde is useful for improving the wet fastness of direct dyes on cotton and as an optical bleaching agent.[26]

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[24] *BIOS* **259**; **1088**; *FIAT* **1302**; Landolt, *Am. Dyestuff Reporter* **38**, 353 (1949); ICI, BP 472,473; 580,205. See also Petersen, *Angew. Chem.* **61**, 17 (1949).

[25] IG, SP 224,613. See also Adams, Wilson and ICI, BP 624,051–2.

[26] Geigy, BP 595,065.

Chapter XXI

AZO DYES FOR CELLULOSE ACETATE

The hydroxyl groups in cellulose have an essential function in the affinity of dyes for cellulose, and cellulose acetate, as an ester of cellulose, differs from cellulose in its dyeing properties. Among the commercial dyes for cotton, wool and silk, there were a few acid, basic and basic-mordant dyes which had some affinity for cellulose acetate, and these were used in the early days although they were unsatisfactory.[1] By giving a preliminary swelling treatment with cellosolve, acetate rayon can be dyed with direct cotton dyes, acid dyes, solubilized vat dyes, and azoics.[2] Another method for dyeing cellulose acetate rayon is to saponify the acetyl groups with hot alkaline solutions, and dye the cellulose thus regenerated with dyes suitable for cotton and viscose. In view of the difficulty of obtaining a homogeneous product at the end of the saponification process and the danger of weakening the fiber, the process is now used only for very special purposes.

The Ionamines

Green made the first systematic study of the properties of dyestuffs which could be applied to cellulose acetate by a direct dyeing process, and he concluded that the presence of hydroxyl and amino groups, a low molecular weight and a nearly neutral or basic character were advantageous, and conversely, that a comparatively large molecular weight, acid character (e.g., the presence of sulfonic groups) and high solubility in water were unsuitable. The present range of cellulose acetate dyes [3-11a] is much wider than these limitations would indicate, but as a result of this examination of the dyeing properties of cellulose acetate, Green and Saunders[12] in 1922 discovered the Ionamines (BDC), which were ω-sulfonic acids of *N*-alkylaminoazo compounds (and for blues, of aminoanthraquinone derivatives).[9] They were prepared by (*a*) condensing an insoluble azo dye containing a primary or secondary amino group with formaldehyde-bisulfite;

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[1] Sanderson, *J. Soc. Dyers Colourists* **38,** 162 (1922).

[2] Bowen *et al.*, BP 601,706.

[3-8] As Refs. 1-6 in Chapter XII.

[9] See also Chapter XXVII.

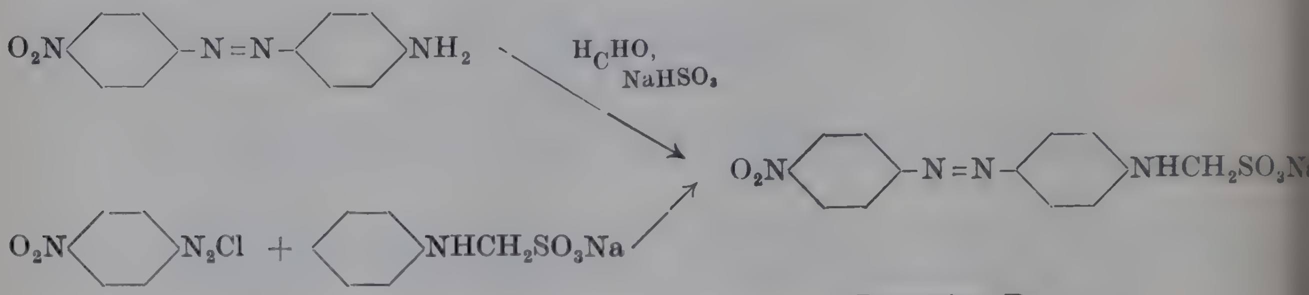
[10] Mullin, Acetate Silk and its Dyes, Van Nostrand Co., New York, 1927.

[11] Green in Thorpe's Dictionary of Applied Chemistry, 4th ed., Vol. I, Longmans, London, 1937.

[11a] Knight, *J. Soc. Dyers Colourists*, **66,** 175 (1950).

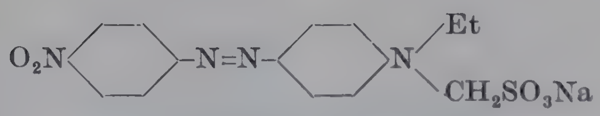
[12] *J. Soc. Dyers Colourists* **39,** 10 (1923); **40,** 138 (1924).

or (*b*) more conveniently, by coupling a diazonium salt with an *N*-methylaniline-ω-sulfonate. The product was soluble in water and stable

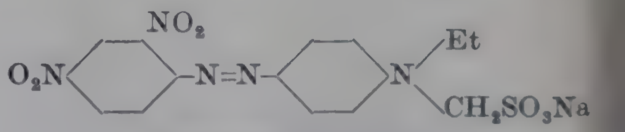


Ionamine B

under neutral conditions, and it was applied to cellulose acetate from a warm, weakly acid or alkaline bath; during the dyeing process it was hydrolyzed to the original aminoazo compound, which was absorbed by the fiber. If the parent azo compound contained a primary amino group, it could be diazotized on the fiber and developed with coupling components such as resorcinol, β-naphthol and *m*-phenylenediamine. The shades directly obtained from the Ionamines of the azo series were yellow to red, while shades from red to brown, blue and black could be produced by diazotization on the fiber and development. Ionamines such as Ionamine Orange CB and Red KA, which were prepared from and liberated a secondary amine

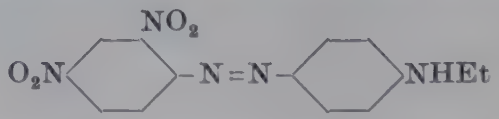


Ionamine Orange CB



Ionamine Red KA

(e.g., I) on hydrolysis, gave only the corresponding shade. Ionamine Yellow



(I)

MA, the *m*-nitroaniline analog of Ionamine B, was used for the direct yellow it gave, although the dye on the fiber had a diazotizable amino group.

Although the Ionamines gave shades on cellulose acetate which had good fastness to washing, light and rubbing, much more satisfactory dyes of a wider range of hues are now available and the Ionamines are obsolete, since there are difficulties in the dyeing process, especially in the use of mixtures and in matching shades, because of differences in the rates of hydrolysis. As soon as it was realised that the Ionamines underwent hydrolysis to the free base before absorption by the fiber, it was clear that cellulose acetate behaved as a solvent towards basic compounds, and Meyer[13] showed that substances which can be extracted from aqueous solution by means of ethyl acetate were absorbed by cellulose acetate. Simultaneously with Green's work, Clavel[14] found basic dyes such as Auramine, several of the triphenylmethane colors, the Gallocyanines and the Safranines could be applied to cellulose acetate like a direct cotton dye to cotton from a hot solution with the addition of salts. The fastness to light was better than on cotton, but these dyes again are no longer of interest to the cellulose acetate dyer since much faster dyes are available. The rapid development that has taken place in cellulose acetate dyes has resulted from the observation that both water-soluble and water-insoluble dyes are applicable to cellulose acetate, provided the dyes can be offered as aqueous dispersions or solubility in water is produced without loss of solubility in (or affinity for) the cellulose ester. Thus sulfonic groups can be present in certain positions, as in the nitro dyes cited in Chapter X and the azo dyes (2,6-dinitroaniline-4-sulfonic acid——→α or β-naphthylamine or their *N*-ethyl derivatives) and (aniline ——→phenyl-peri-acid).[15] Cellit Fast Red B and BB (By) have been stated to be (2,4-dinitroaniline——→*N*-benzylorthanilic acid) and (*p*-nitroaniline ——→*N*-ethyl-*N*-*m*-sulfobenzyl-*m*-toluidine) respectively.[8] Carboxyl and sulfuric ester (-O-SO_3Na) groups, which improve the solubility in water without lowering the solubility in ester solvents, can be present with advantage. The special ranges of dyes now used for cellulose acetate consist mainly of aqueous dispersions of insoluble or sparingly soluble azo and anthraquinone dyes.[9]

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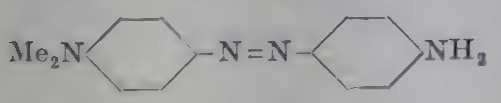
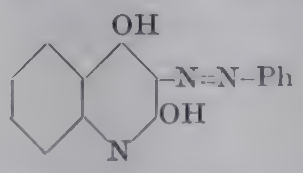
[13] *Melliand Textilber.* 6, 737 (1925).

DISPERSED DYES

The first groups of dispersed dyes for cellulose acetate were the Dispersols[16] and the S.R.A. colors;[17] the latter name indicates colloidalization with the aid of sulforicinoleic acid, which has now been replaced by far more powerful dispersing agents such as the condensation products of alkylnaphthalenesulfonic acids with formaldehyde. The older representatives are aminoazo compounds of the type employed for the Ionamines;



Dispersol Diazo Black AS



Dispersol Yellow 3G

as with the Ionamines, the Dispersol dyes possessing primary amino groups can be diazotized and developed on the fiber. Thus Dispersol Diazo Black AS is identical with the amine of which the formaldehyde-bisulfite derivative was Ionamine A or Black AS; it dyes cellulose acetate yellow directly, and by diazotization on the fiber and development with hydroxynaphthoic acid a full blue-black with excellent fastness properties is produced. While these simpler azo compounds are still in use, faster dyes and dyes more readily amenable to dispersion in water have been synthesized.

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[14] DRP 355,533.

[15] Bayer, BP 225,862; British Dyestuffs and Frank, BP 226,948.

[8] See p. 637.

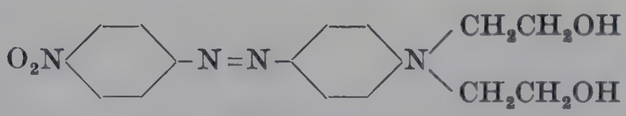
[9] See p. 637.

[16] Baddiley, Shepherdson and British Dyestuffs, BP 211,720.

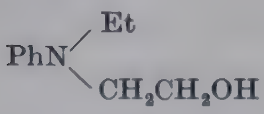
[17] Ellis and British Celanese, BP 219,349.

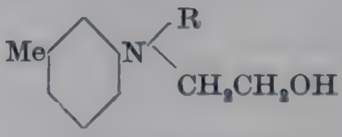
Most of the earlier yellow and orange azo dyes for acetate silk are phototropic, darkening or changing in shade on exposure to light. Green and Saunders found that while the yellow aminoazobenzene derivatives as a class exhibit this property when dyed on acetate rayon, the effect is more marked with the greener shades. The aminoazo dyes which are phototropic on cellulose acetate, ethyl cellulose and benzyl cellulose do not exhibit the property on cellulose and nitrocellulose.[18] Negative substituents hinder the phototropic effect. The active rays of light are the extreme visible violet; ultraviolet and blue to infrared are without action. Phototropy seems to be caused " not by a simple modification of the electronic structure of the dye, but by a change involving heavier particles."[18] Dispersol Yellow 3G (BDC) (aniline⟶2,4-dihydroxyquinoline) dyes cellulose acetate a bright lemon-yellow, free from the defect of phototropism.[11]

An ethanolamine group in an insoluble azo compound is an aid to colloidalization. As early as 1923, Green and Saunders had prepared azo dyes from phenyl diethanolamine $PhN(CH_2CH_2OH)_2$ and similar bases, and

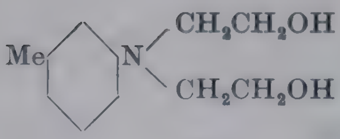

Dispersol Fast Red R

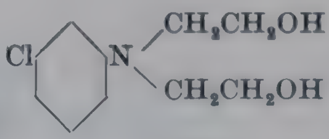
shown their value as acetate silk dyes.[12] The Dispersol (ICI) and the Celliton (IG) groups include dyes prepared from similar hydroxyalkylanilines (e.g., II-VIII). When these are coupled with diazotized *p*-nitroanilines, the

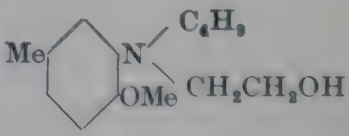

(II)


(III ; IV ; VII)

(III ; $R=H$)
(IV ; $R=Me$)
(VII ; $R=n\text{-}C_4H_9$)


(V)


(VI)


(VIII)

chloronitroanilines, etc., orange to bluish-red dyes with excellent fastness properties are obtained. An important development was the observation that 6-chloro- and 6-bromo-2,4-dinitroaniline as the diazonium components gave blue monoazo dyes, which were dischargeable (cf. the Celliton Discharge Blues).[19]

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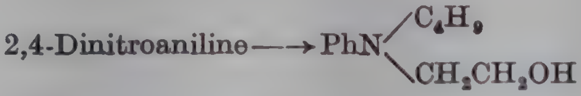
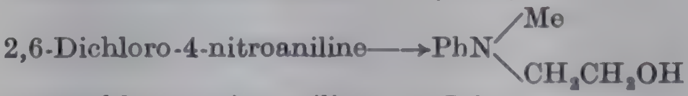
[18] Mechel and Stauffer, *Helv. Chim. Acta* **24,** 151E (1941). See also Chapter XL in Vol. II.

[11] See p. 637.

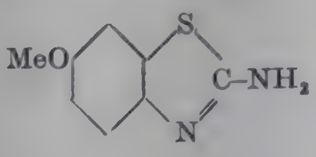
[12] See p. 637.

TABLE I

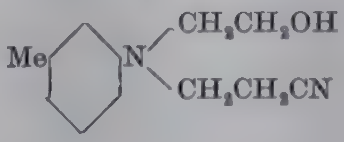
CELLITON DYES

Celliton	*Constitution*
Fast Yellow G	*p*-Aminoacetanilide ⟶ *p*-Cresol
Fast Yellow 5R	*p*-Aminoazobenzene ⟶ *o*-Cresol
Yellow 3GN	*o*- and *p*-Nitroaniline ⟶ (XI)
Yellow 5G	*m*-Nitroaniline ⟶ (XI)
Fast Orange GR	*p*-Nitroaniline ⟶ Aniline
Fast Orange 5R	*p*-Nitroaniline ⟶ Diphenylamine
Fast Scarlet RN	*p*-Nitroaniline ⟶ (X)
Scarlet B	*p*-Nitroaniline ⟶ (II)
Fast Red GG	*p*-Nitroaniline ⟶ (V)
Red R[7]	*p*-Nitroaniline ⟶ (III)
Fast Red R[7]	*p*-Nitroaniline ⟶ (VI)
Fast Rubine B	2-Chloro-4-nitroaniline ⟶ (II)
Fast Rubine 3B	2-Chloro-4-nitroaniline ⟶ (V)
Rubine BBF	5-Nitro-2-aminophenol ⟶ (V)
Discharge Rose B1521[4]	
Red Violet RR	 $\text{2,4-Dinitroaniline} \longrightarrow \text{PhN}\begin{matrix}\diagup C_4H_9 \\ \diagdown CH_2CH_2OH\end{matrix}$
Discharge Violet RR	
Violet R[7]	2,4-Dinitroaniline ⟶ (VII)
Discharge Pink BRF	(IX) ⟶ $PhN(CH_2CH_2OH)_2$
Discharge Blue FFR	6-Bromo-2,4-dinitroaniline ⟶ (XII)
Blue RRF	
Discharge Blue 3G	2-Chloro-4-nitroaniline $\xrightarrow{\text{acid}}$ (XIII)
Discharge Blue 5G	(IX) ⟶ (XIII)
Discharge Blue BG	6-Bromo-2,4-dinitroaniline ⟶ (XIV)
Discharge Blue 3R[7]	6-Bromo-2,4-dinitroaniline ⟶ (VIII)
Fast Brown 3R	 $\text{2,6-Dichloro-4-nitroaniline} \longrightarrow \text{PhN}\begin{matrix}\diagup Me \\ \diagdown CH_2CH_2OH\end{matrix}$
Fast Brown 5R[20]	2,6-Dichloro-4-nitroaniline ⟶ (IV)

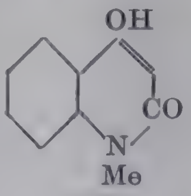
The constitution of a series of Celliton colors (IG) is stated in Table I.[3, 9] The Celliton range provides examples of varied types of azoic dyes for cellulose acetate. The diazonium components are nitroanilines and their derivatives, the only amine of a distinct type being 2-amino-6-methoxy-



(IX)



(X)



(XI)

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[19] IG, BP 409,921; ICI, BP 421,975; Geigy, BP 462,233.

[7] See p. 637.

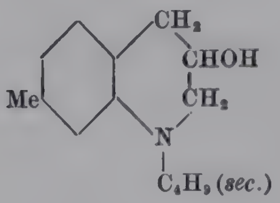
[4] See p. 637.

[20] *FIAT* 1313 III gives (VIII; H in place of C_4H_9) as the coupling component.

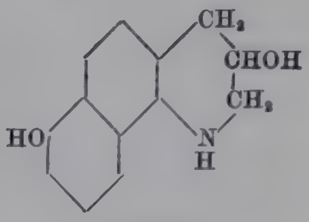
[3] See p. 637.

[9] See p. 637.

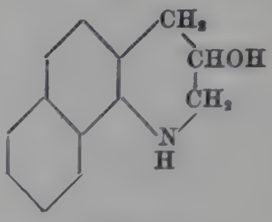
benzothiazole (IX). In addition to the ethanolamine derivatives (II)-(VIII), the special coupling components are the cyanoethyl derivative (X), the α-quinolone (XI), and the tetrahydroquinoline derivatives (XII), (XIII) and (XIV). The tetrahydroquinoline derivatives are prepared by condensing the appropriate amine (e.g., 1-amino-5-naphthol for XIII) with epichlorhydrin.[19a]



(XII)



(XIII)



(XIV)

The dispersed azo dyes which contained free amino groups, so that the dyes could be diazotized on the fiber and developed, were marketed by the IG as Cellitazols. The constitution of a series of Cellitazols is stated in Table II; the asterisk indicates that the nitro group is reduced to the amino group by means of sodium sulfide.

TABLE II

Cellitazol	*Constitution*
8R	α-Naphthylamine
ORB (Cellit Fast Yellow 2GN)	*m*-Aminobenzoic acid——→*o*-Anisidine
R	Aminoazobenzene
B	Dianisidine
BGL[21]	3,3′-Dimethoxy-4,4′-diaminoazobenzene
STN	*p*-Nitroaniline——→α-Naphthylamine*
Diazo Blue	*p*-Nitroaniline——→4-Ethoxy-*m*-toluidine*
AZN(AL)	2-Chloro-4-nitroaniline——→Dimethylaniline*
BT	*p*-Nitroaniline——→Cresidine*
B5266	*p*-Nitroaniline——→Diethylaniline*
27556	*p*-Nitroaniline——→α-Aminotetralin*
GG	5-Nitro-*o*-anisidine——→(V)*

Recent patents on azo dyes for cellulose acetate represent only minor variations in the known types. One object is the discovery of violet and blue dyes with resistance to burnt gas fumes.[9] The yellow dye (3,5-dinitroaniline——→aniline) and the orange-yellow dye (5-nitro-*o*-anisidine——→ *m*-5-xylenol) are nonphototropic.[22] *p*-Aminoazobenzenes containing three or four substituents *ortho* to the azo group dye cellulose esters and ethers in golden yellow shades.[23] Mononitration of 4-aminoazobenzene substituted by Cl, NO_2 or NMe_2 in the 4′-position yields fast yellow to yellow-brown dyes.[24] The black pigment obtained by coupling tetrazotized 4,4′-diamino-2-methylphenyl-1,1′-azonaphthalene with 2-hydroxy-3-naphthoic acid in aqueous sodium acetate has a special yield (color value) and light fastness.[25] Several patents relate to fluorescent dyes which are fast to light and washing; e.g., when the red dye 2,4-dinitrobenzeneazodiethylaniline is treated on the fiber with an aqueous alcoholic solution of sodium sulfoxylate-formaldehyde, the shade changes to yellow, which appears blue-green in ultraviolet light.[26] Half esters of oxalic acid such as $Ph\text{-}NEt\text{-}CH_2CH_2\text{-}O\text{-}COCOOH$ are useful coupling components.[27] The dye (*p*-amino-*N*-β-hydroxyethylbenzamide → phenylmethylpyrazolone) is heated with maleic anhydride.[28] Arylamines of the benzene, naphthalene and benzothiazole series, in which the amino group carries a $\text{-}CH_2\text{-}CHOH\text{-}CH_2OH$ group, have been suggested as coupling components.[29] A compound of this type leading to an *o*-aminoazo dye is

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[19a] IG, BP 449,089; 456,824; 458,423.

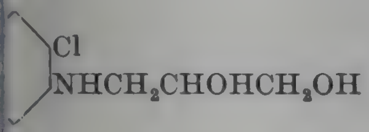
[21] *FIAT* 1313 III.

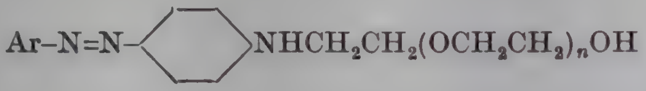
[9] See p. 637.

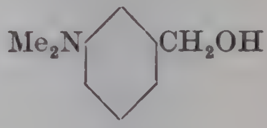
[22] Ciba, BP 584,731; ICI, BP 407,037.

[23] Wright and British Celanese, USP 2,423,542.

[24] Ciba, SP 218,273-5.


(XV)


(XVI)


(XVII)

(XV).[30] The component may contain an $N(CH_2\text{-}CHOH\text{-}CH_2OH)_2$ group.[31] Yellow, red and blue azo dyes (XVI) have been described which contain polyethyleneglycol chains.[32] *m*-Dialkylaminobenzyl alcohols (e.g., XVII), in which an alkyl, hydroxyalkyl or glyceryl radical may be attached to the nitrogen atom may be used as second components. The dye (*p*-nitroaniline → XVII) dyes a fast red.[33] The alkanol group may be attached to a sulfonamido group in the first component, as in $H_2N\text{-}C_6H_4\text{-}SO_2NHCH_2CH_2OH$.[34] Dyes such as ($Me_2NCH_2CONHC_6H_4NH_2$ → *p*-alkylphenol) give yellow to yellow-brown shades of good fastness to light and washing.[35] Azo dyes containing a trifluoroacetamido group are useful for natural and synthetic protein fibers, as well as cellulose acetate.[36] Trifluoromethyl derivatives of tetrahydroquinoline and benzomorpholine are useful as coupling components.[37] Monoazo dyes containing a 1,3-butadiene group (e.g., *p*-nitroaniline → *N*-1-methyleneallylaniline) can be polymerized on the fiber to yield an extremely wash-resistant dye.[37a]

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[25] Ciba, SP 215,403. See also Kuhlmann, BP 602,878.

[26] Ward, Salvin and Celanese Corp., USP 2,433,939.

[27] Ciba, SP 215,068–075.

[28] Ciba, SP 216,416. See also SP 229,185.

[29] Dickey, McNally and Eastman Kodak, USP 2,323,314–5.

[30] Dickey, Byers and Eastman Kodak, USP 2,271,220.

[31] McNally, Dickey and Eastman Kodak, USP 2,336,275; see also Eastman Kodak, USP 2,448,853.

[32] Dickey, McNally and Eastman Kodak, USP 2,359,305. See also ICI, BP 434,126.

[33] McNally, Dickey and Eastman Kodak, USP 2,196,221.

[34] Ciba, BP 543,567.

[35] McNally, Dickey and Eastman Kodak, USP 2,436,115.

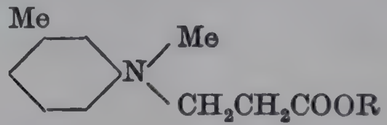
[36] Dickey and Eastman Kodak, USP 2,436,100. See also USP 2,342,678; 2,432,393.

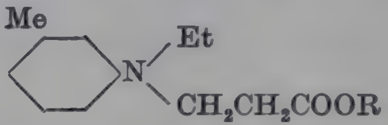
[37] Dickey, McNally and Eastman Kodak, USP 2,442,345. See also USP 2,491,481.

[37a] Dickey and Eastman Kodak, USP 2,469,682.

Amino acids, such as Ph-NMe-CH_2CH_2COOH, prepared by the addition of monomethylaniline to acrylic acid, and its β-hydroxyethyl ester, are suitable second components for water-soluble acetate rayon dyes and the IG had scheduled a series of these dyes for manufacture.[3,5] Thus Acetate Silk Scarlet 5892 was the mixed dye (*p*-nitroaniline⟶Ph-NMe-CH_2CH_2-COOH + Ph-NMe-$CH_2CH_2COOCH_2CH_2OH$). Other shades were obtained by changing the diazonium component, and by using (XVIII) and (XIX) as coupling components. Each dye consisted of a mixture of 0.7 mole of the dye from the acid (R = H) and 0.3 mole of the dye from the ester

(XVIII)

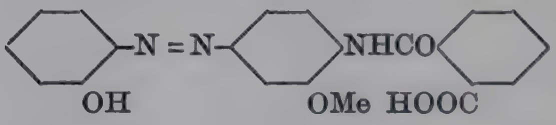




(XIX)

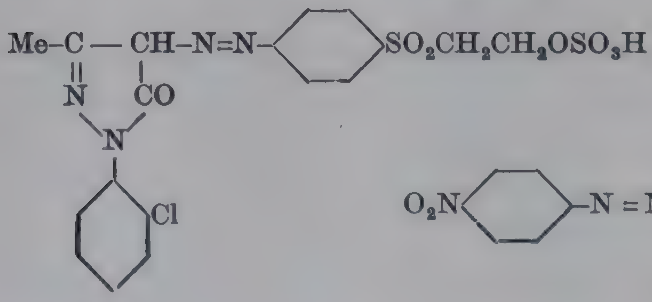
(R = CH_2CH_2OH). Acetate Silk Red was (*p*-nitroaniline⟶XIX); Re Violet (2,4-dinitroaniline⟶XVIII); Rubine (2-chloro-4-nitroaniline⟶ XIX); and Brown (2,6-dichloro-4-nitroaniline⟶XVIII).

Azo dyes such as (XX), derived from phthalic and other dicarboxyli

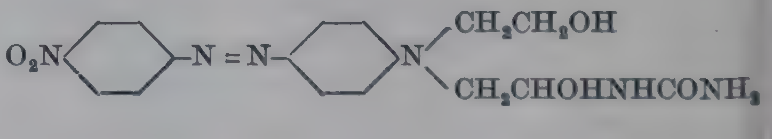


(XX)

acids, dye cellulose acetate, as well as wool and silk.[38] The dye (XXI) dye cellulose acetate in powerful greenish yellow shades; by treatment wit



(XXI)



(XXII)

succinic anhydride in glacial acetic acid, the SO_3H group is replaced b $COCH_2CH_2COOH$ and the product dyes fast, nonphototropic, pure yello shades.[39] Dyes containing alcoholic and ureido groups have been describe which are stated to be useful for acetate silk, wool, silk and nylon, and t be fast to light, washing and gas fading. An example is the red dye (XXII).

Heterocylic intermediates, both as the diazonium and coupling con ponents, figure prominently in recent patents, particularly those of t Eastman Kodak Co., who have marketed the Eastone dyes for cellulo

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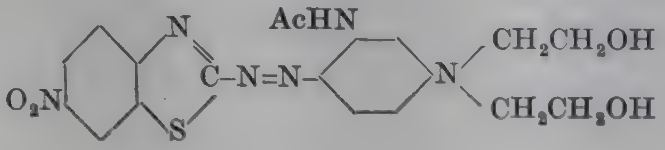
[3] See p. 637. [5] See p. 637. [38] Felix, Heckendorn and Ciba, USP 2,398,3

[39] Müller, Scheidegger and Ciba, USP 2,424,493.

[40] Dickey, McNally and Eastman Kodak, USP 2,397,927.

acetate. The reddish blue dye (XXIII) is claimed to be fast to light and gas fumes (cf. Discharge Pink BRF and Blue 5G).[41] Dyes produced from suitable pyrazolones as coupling components are fast to light and have



(XXIII)

high tinctorial power.[42] By coupling a diazotized amine, R-CO-C_6H_4-NH_2 in which R is a furan, thiophene or pyrrole nucleus, with dimethyldihydroresorcinol (5,5-dimethylcyclohexane-1,3-dione), greenish-yellow dyes are obtained.[43] An alkylenedioxy group appears to offer advantages. The dye (4-aminocatechol ethylene ether⟶*p*-cresol) dyes cellulose acetate fast yellow shades.[44] 2-Aminobenzoxazole and its derivatives are suitable first components for the preparation of cellulose acetate dyes.[45] 1,2,3,4-Tetrahydroquinoline and its derivatives couple with diazonium salts *para* to the nitrogen, and the azo dyes, not containing a sulfonic group, are useful for cellulose acetate (cf. Table I).[46] Monoazo dyes using benzotriazoles, benzomorpholines, benzothiomorpholines, 1-alkylindoles or naphthindoles, and tetrahydrophenanthrolines, have been described.[47] The use of specific diazonium components, such as *p*-nitroaniline derivatives containing sulfonamido, alkylsulfonyl, ketonic, halogen and other substituents, is also the subject of several of these patents, the objects as usual being the production of dyes of a more extensive range of hues and with improved fastness to light and resistance to gas fading.

PeCe is a synthetic fiber made by IG from chlorinated polyvinyl chloride,[47a] and IG had developed a series of dyes, insoluble in water and soluble in organic solvents, which could be dispersed in water and applied to PeCe fiber.[5] There is thus no difference in principle between these dyes and the cellulose acetate dyes, as illustrated by the following examples.

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[41] British Celanese, BP 587,134. See also IG, BP 440,113.

[42] Eastman Kodak, USP 2,439,798.

[43] Eastman Kodak, USP 2,171,159; 2,193,037. See also IG, BP 461,965; Geigy, BP 470,436.

[44] Ciba, BP 580,092.

[45] McNally, Dickey and Eastman Kodak, USP 2,193,037.

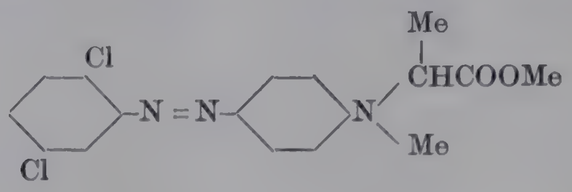
[46] McNally, Dickey and Eastman Kodak, BP 548,902-3.

[47] Eastman Kodak, BP 570,561; USP 2,196,222; 2,198,002; 2,196,776; 2,448,869–70. See also USP 2,130,358; 2,140,537–9; 2,140,987; 2,150,180; 2,186,629; 2,196,757; 2,199,987; 2,206,885; 2,221,020; 2,221,028; 2,226,174 ; 2,226,198; 2,231,705; 2,234,723–4; 2,245,261–2; 2,251,947; 2,258,977; 2,261,176; 2,282,333; 2,283,220; 2,317,365; 2,319,217; 2,322,925; 2,323,315; 2,341,427; 2,364,351; 2,391,886.

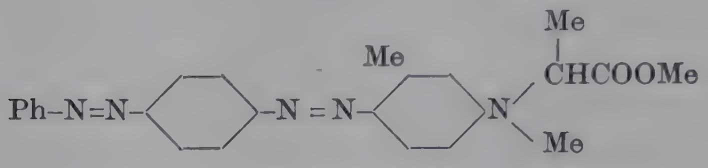
[47a] De Bell, Goggin and Gloor, German Plastics Practice, De Bell and Richardson, Springfield, Mass., 1946.

[5] See p. 637.

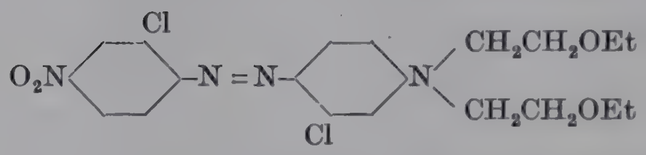
For blue and violet shades in fact, the cellulose acetate dyes available in the commercial range were employed.



PeCe Yellow N



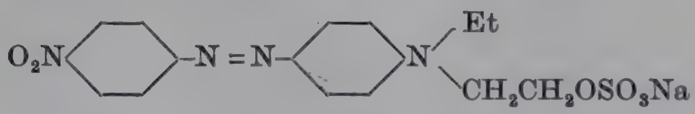
PeCe Scarlet N



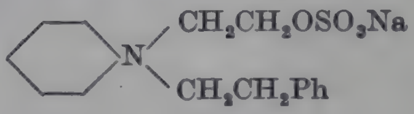
PeCe Red N

THE SOLACET DYES (ICI)

The Solacet dyes (ICI) are a valuable addition to the range of dyes available for cellulose acetate.[11] They are not aqueous dispersions of insoluble dyes, but sulfuric esters of ethanolamine derivatives such as (I). The sodium salt (I) is soluble in water without prejudice to the properties responsible for affinity for cellulose acetate. Being sodium alkyl sulfates, these compounds are distinct from the Ionamines, which are unstable both to acid and alkali and hydrolyze in the dyebath. The Solacets undergo no chemical change during the dyeing process, which is therefore quite analogous to the dyeing of cellulose fibers with direct dyes; the analogy with the direct cotton dyes extends to their salt sensitivity; the dyeing process is controlled and the desired exhaustion obtained by the addition of common salt or Glauber salt. The sodium alkyl sulfate group imparts surface activity to the dye molecule, so that penetration is improved, and the Solacet dyes are particularly valuable for obtaining good penetration and level dyeing of tightly woven fabrics.



(I)



(II)

In preparing a Solacet dye, an azo dye containing a hydroxyethyl group may be sulfated, or the sulfuric ester group may be present in the component to be coupled with a diazonium salt.[48] In place of ethyl and ethanolamine groups, longer alkyl chains may be employed; thus diazotized *p*-nitroaniline may be coupled with the tertiary amine Ph-NR-CH_2CH_2-O-SO_3H, in which R = *n*-amyl, hexyl or octyl.[48] Red dyes of the type of (I) have superior affinity for acetate rayon from dilute solution if the sum of the carbon atoms in the two alkyl groups is between 6 and 11. 2-Cyano-4-nitroaniline and its 6-chloro and 6-bromo derivatives, on diazotization and coupling with sulfuric esters of *N*-hydroxyalkylanilines such as (II), yield dyes with high affinity for cellulose acetate and nylon and good fastness properties.[49] An example of a Solacet dye, using a phenoxyethyl group in addition to the hydroxyethyl group which is sulfated, is (III).[50] The yellow dyes (H_2N-C_6H_4-$OCH_2CH_2OSO_3Na$ ⟶ 2-hydroxydibenzofuran) are fast to light on cellulose acetate and nylon.[51]

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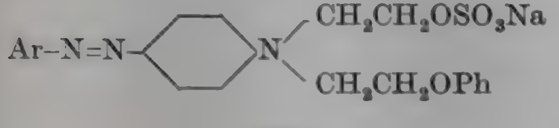
[11] See p. 637.

[48] Knight *et al.* and ICI, BP 429,936; 430,079; 431,564; 441,089; 455,643; 466,799; 486,302; 492,668; 558,330; 575,342; 588,409; 609,275; USP 2,473,885. See also Ciba, SP 236,764; 238,460–6; Kuhlmann, BP 478,228; 489,738; British Celanese, BP 516,929.



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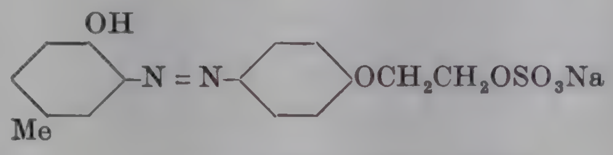
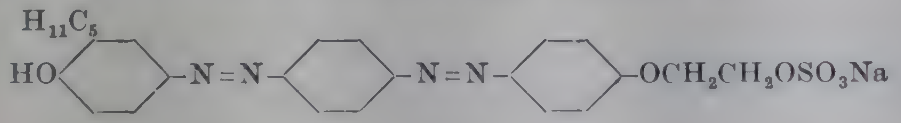
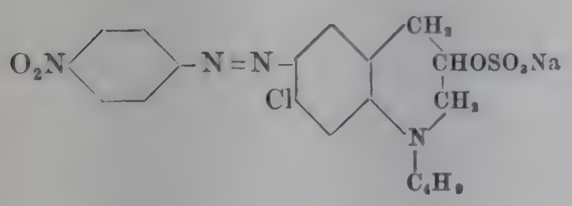


Acetate Silk Yellow 66833

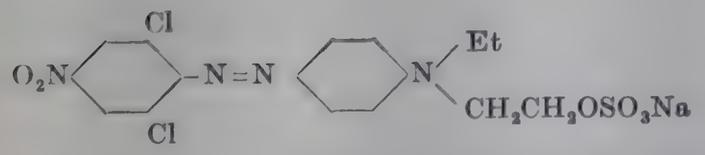
Among the members of the Solacet Fast range may be mentioned Yellow G, Orange 2G, Scarlet B, Rubine 3B and Violet 4R. Acetate Silk Yellow 66833 (IG) is a Solacet type of color in which the ethanol sulfate group is in the diazonium component, and is one of several found by IG to be suitable for dyeing crepes and heavy, tightly woven acetate rayon fabrics.[5] This dyestuff has been described in ICI patents. Further examples of dyes of the Solacet type cited in ICI and other patents are:



Orange



Red



Orange-brown

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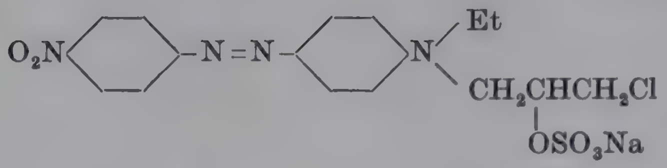
[48] See p. 646.

[49] Green, Saunders and British Dyestuffs, BP 181,750; Perkin, Bates and British Dyestuffs, BP 237,739; Ciba, BP 447,561; 505,854; Heywood and ICI, BP 584,692; USP 2,474,737.

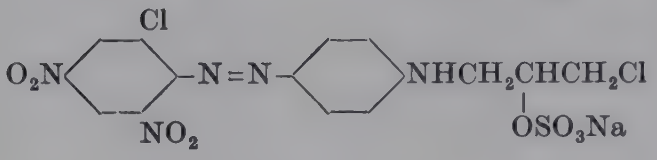
[50] Heywood and ICI, BP 584,956.

[51] Heywood, Knight and ICI, BP 596,280.

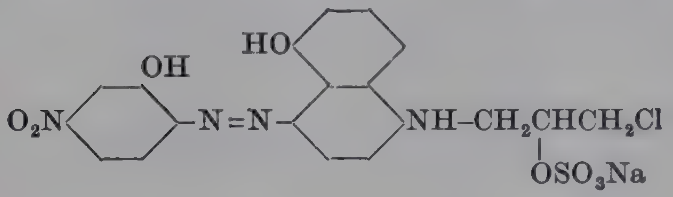
[5] See p. 637.



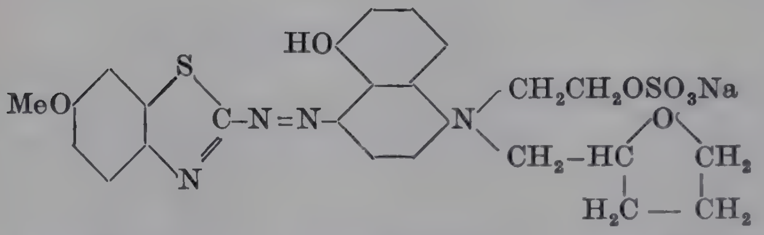
Scarlet



Violet

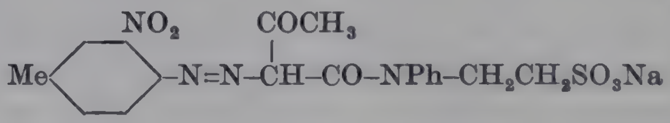


Blue



Blue

A sulfoethyl (e.g., -NEt-$CH_2CH_2SO_3Na$) group may be used for solubilization; unlike the sulfomethyl group in the Ionamines, the sulfoethyl group is stable under the conditions of dyeing and the shade on the fiber is that of the water-soluble dye. An example of a yellow dye of this type is claimed to



$$\text{Me}\overset{\text{NO}_2}{\text{C}_6\text{H}_3}\text{-N=N-}\overset{\text{COCH}_3}{\text{CH}}\text{-CO-NPh-CH}_2\text{CH}_2\text{SO}_3\text{Na}$$

have good fastness to light, washing and gas fumes.[52] Sulfochloroacetic acid (HO_3S-CHCl-COOH), prepared by heating chloroacetic acid with sulfur trioxide at 140°, is useful for the preparation of water-soluble cellulose acetate dyes; thus, it is heated with a hydroxyalkylaniline to form the acid ester, which is coupled with diazotized *p*-nitroaniline, or an azo dye from a hydroxyalkylaniline is esterified with sulfochloroacetic acid.[53] An example is the sulfochloroacetic ester of the blue monoazo dye (2,4-dinitro-6-cyanoaniline⟶*N*-methyl-*N*-β-hydroxyethyl-*m*-toluidine). Water-soluble dyes containing aromatic sulfonic groups, such as (A⟶2,4-dihydroxyquinolinesulfonic acid), have been suggested for application to cellulose acetate.[54]

The use of sodium alkyl sulfates has been followed by patents on thiosulfuric, phosphoric and other esters of inorganic acids. Azo dyes of the form Ph-N =N-Ar-NR^1-$(CH_2)_n$-O-PO(OR^2)-OM, in which R^1 and R^2 are alkyl groups, and M is H or a cation giving solubility in water, are dyes for cellulose acetate; instead of phosphoric, thiophosphoric esters can be used, and the same patent often covers various methods of solubilization.[55] It is doubtful if methods other than sulfation offer any advantages, and the fastness properties appear in fact to be altered unfavorably.

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[52] Knight and ICI, BP 441,884; Eastman Kodak, USP 2,251,921.

[53] Ciba, SP 225,362; 227,509–15; 231,254; BP 565,697.

[54] Geigy, BP 455,216; 441,628.

DYEING METHOD

Dispersed dyes are applied to cellulose acetate from a soap bath at 60–80°; raising the temperature to over 80° is liable to diminish the luster of the rayon. The function of soap is not only to maintain the insoluble dye as a stable dispersion, but also to swell the fiber so that it can absorb the dye more readily. The absorption varies within the narrow limits of 0.25 to 1% on the weight of the fiber.

The difference between cellulose and cellulose acetate in their affinity for dyes, which was originally regarded as a serious problem in dyeing acetate silk, is now utilized for producing two-color effects on union fabrics of acetate silk and cotton or viscose. Dispersed dyes of the Dispersol, Celliton, Cibacet and similar types are suitable for such differential dyeing, since they leave the cellulose fiber undyed. Many cellulose acetate dyes are suitable for dyeing nylon, and patent claims frequently cover both the fibers.

The solubility of azoic dyes for cellulose acetate in acetone, cellosolve and other solvents may be utilized for spun dyeing or mass pigmentation methods (see Chapter VI). Azo compounds containing long paraffin chains which impart the requisite solubility in acetone have been suggested. Thus the hydroxyl group in the blue disazo compound (*p*-nitroaniline ⟶ 2,5-dimethoxyaniline ⟶ *m*-5-xylenol) is methylated, the nitro group is reduced, and the primary amine is diazotized and coupled with *m*-stearamidodiethylaniline.[56]

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[55] Eastman Kodak, USP 2,183,998–9; 2,196,757; 2,196,776; 2,198,002; 2.221,027; 2,227,963; 2,328,570. See also IG, BP 486,097; 490,945; Ciba, BP 510,453.

[56] British Celanese, BP 551,435–7. See also BP 599,278; 599,562.

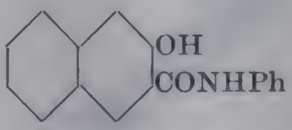
CHAPTER XXII

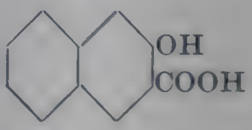
AZOIC DYES

The use of Para Red (1-*p*-nitrobenzeneazo-2-naphthol) and similar organic pigments of the azo class for coloring oils and varnishes and for making lakes in paint manufacture is well known. Read Holliday and Son in 1880 made an important advance in dyeing methods when they found that cotton, impregnated with alkaline β-naphthol, dried and developed with diazotized *p*-nitroaniline, was dyed a deep red, as bright as the much costlier Turkey Red. Para Red thus produced on the fiber was soon followed by other insoluble azo colors derived from β-naphthol and other diazonium salts—bordeaux or claret from α-naphthylamine and orange from *o*- and *m*-nitroaniline. Blue was produced by means of tetrazotized dianisidine, the inclusion of a fatty acid and a copper salt being necessary for obtaining the true blue shade, which was faster to light than indigo on cotton, but not fast to acids. 6- and 7-Amino-1-naphthol (Naphthol BD and 3B) (C) were used for producing blacks with diazotized *p*-nitroaniline. The insoluble azo dyes produced on the fiber, once called ice colors because ice was used for the diazotization of the amines, are now known as azoic dyes,[1] to distinguish them from the water-soluble azo dyes applicable to fibers by ordinary dyeing processes.

The azoic dyeings from β-naphthol had many limitations, such as the lack of substantivity of β-naphthol for cotton, the narrow range of shades obtainable from a single coupling component, and the poor fastness to light and rubbing. Being cheap, however, Para Red continues to be used in calico printing, especially in discharge styles; the non-colloidal character of alkaline solutions of β-naphthol and the low substantivity can be remedied to some extent by the addition of wetting agents and protective colloids to the impregnating bath. The discovery of Naphtol AS (GrE; 1911), the anilide of 2-hydroxy-3-naphthoic acid (β-oxynaphthoic or BON acid; I),

Naphtol AS





(I)

as a dye component utilizable by a simplified Para Red technique because of its substantivity for cotton, was far-reaching, although the compound itself had been made twenty years earlier by Schöpff. It has vastly extended the scope of azoic colors, as Naphtol AS can be replaced by other arylides of BON acid and by arylides of other *o*-hydroxycarboxylic acids. The azoics constitute about a fifth of the dyes in commercial use. There are at present some 30 naphthols and 50 bases[2–4] and stabilized diazonium salts on the market, so that about 1,500 combinations from yellow through green and blue to black are possible. Of these, however, only a small fraction is commonly employed, because many of the shades overlap, the fastness is not of the requisite standard, and for other reasons; thus, among the thirty or more Naphtols and their analogs made by other manufacturers (to which may be added hundreds of such compounds mentioned in patents), the anilide of BON acid is still the most largely used. The dyes produced on the fiber from the arylamides of BON acid are greatly superior to the azoics from β-naphthol in fastness to rubbing (crocking), washing and light. Combinations are available which are fast enough to light to be used for casement curtains, and to kier boiling and bleaching to enable them to be dyed on yarn which is to be woven with undyed yarn and bleached in the piece. Several azoic dyes can compare favorably with the anthraquinonoid vats in all-round fastness. The azoics are in fact invaluable for deep and brilliant shades of scarlets, reds, maroons and chocolates, while the vats are preferred for blues and greens.

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[1] Lapworth in Thorpe's Dictionary of Applied Chemistry, Vol. IV, 4th ed., Longmans, London, p. 227.

Material advance in naphthol dyeing has been effected by the production of special amines for diazotization and development, and of stabilized diazonium salts. In printing, the " naphthols "[5] are of the utmost importance since they lend themselves to application by a variety of styles. Mixtures of the stabilized diazonium salts with the " naphthols " (Rapid Fasts, Rapidogens, Rapidazols) are available for printing, so that both the components can be applied to the fabric in a single operation. Similar mixtures suitable for dyeing purposes, and azoic dyes prepared in substance and temporarily solubilized or dispersed for use in dyeing and printing, are two probable lines of advance.

CHEMICAL CONSTITUTION OF NAPHTOLS

The Naphtol AS series now comprise two types of coupling components: (1) for all shades other than yellow, arylamides of *o*-hydroxycarboxylic acids in which the second position adjacent to the hydroxyl is free for coupling with diazonium salts; and (2) for yellow shades, acylacetic arylamides which couple on the reactive methylene group. Naphtols of the

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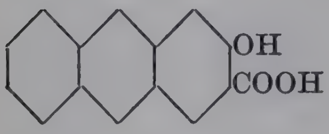
[2-4] IG methods for the preparation of intermediates for Naphtols, a few Naphtols and Fast Bases have been described in (2) *BIOS* **986**; (3) **1149**; and (4) **1363**.

[5] Since " Naphtol " is the IG name for their azoic coupling components, it is used only for the members of the series first made by IG, and for the sake of brevity phenolic and enolic coupling components used in azoic dyeing are referred to in this chapter as " naphthols."

first type are prepared mainly from BON acid (I), the variations being in the arylamine half. The arylides of BON acid are useful for scarlet, red, violet and blue shades, especially reds. Arylides of 2-hydroxyanthracene-3-carboxylic acid (II) are employed for greens, arylides of 3-hydroxydibenzofuran-2-carboxylic acid (III) and 2-hydroxycarbazole-3-carboxylic acid (IV) for browns, and arylides of 2-hydroxy-α-benzocarbazole-3-carboxylic acid (V) for blacks. Attempts have been made to introduce other phenolic coupling components (e.g., 4-benzoyl-1-naphthol), but apparently without success. Table I gives a list of the Naphtols and their constitution stated as the acid and amine which are condensed together. Brenthols are the ICI analogs of the Naphtols. A Brenthol which does not correspond to any of the Naphtols is Brenthol BA, the 5-bromo-2-methoxyanilide of BON acid.[6] Cibanaphtols are the group name of Ciba for the "naphthols", and as shown in Table I, they are mostly constituted similarly to the IG Naphtols. Cibanaphtol RP was an innovation,[7] but the type offered no special advantages and has not been exploited further. Cibanaphtols SB, ST and SD, which are interesting as the only benzene derivatives in this series, yield warm brown shades of good fastness; but they have poor affinity for cotton and have been abandoned.



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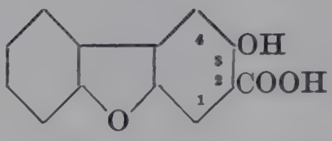

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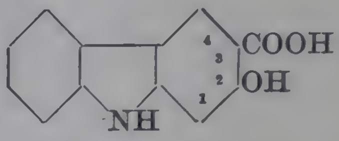

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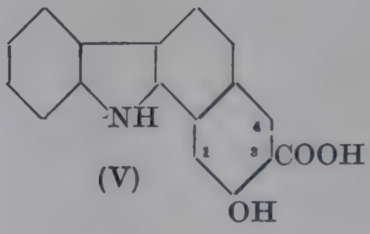
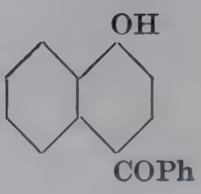
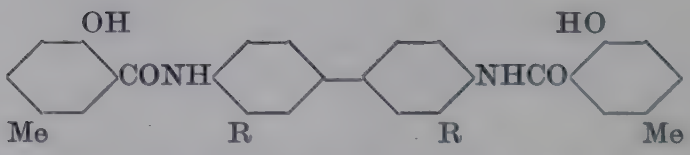


(V)



Cibanaphtol RP



Cibanaphtols SB; ST; SD (R=H; Me; OMe)

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[6] Moualim and Venkataraman, *J. Sci. Ind. Research* (*India*) **3**, 447 (1945).

[7] Lederer, *Melliand Textilber.* **12**, 461 (1931).

TABLE I

NAPHTOLS (IG), BRENTHOLS (ICI) AND CIBANAPHTOLS (CB)

Naphtol	*Brenthol*	*Ciba-naphtol*	*Acid*	*Amine*	*Ref.*
AS	AS	RF	(I)	Aniline	8
AS–D	OT	RTO	(I)	*o*-Toluidine	8, 9
		RT	(I)	*p*-Toluidine	10
AS–OL	FR	RK	(I)	*o*-Anisidine	8, 11
AS–RL	PA	RBL	(I)	*p*-Anisidine	8, 12
		RPH	(I)	*p*-Phenetidine	10
AS–LT	MA		(I)	5-Methoxy-*o*-toluidine	13
AS–BG	FO	RDM	(I)	2,5-Dimethoxyaniline	8, 11
AS–BS	MN	RM	(I)	*m*-Nitroaniline	12, 14
AS–E	BB	RC	(I)	*p*-Chloroaniline	8, 11
AS–TR	CT	RCT	(I)	5-Chloro-*o*-toluidine	8, 9
		RCA	(I)	4-Chloro-*o*-anisidine	15
	BA		(I)	4-Bromo-*o*-anisidine	6
AS–ITR			(I)	3-Chloro-4,6-dimethoxyaniline	16
AS–LC			(I)	4-Chloro-2,5-dimethoxyaniline	17
AS–BO	AN	RN	(I)	α-Naphthylamine	8, 12
AS–SW	BN	RA	(I)	β-Naphthylamine	8, 12
AS–S			(I)	2-Amino-3-methoxydibenzofuran	6, 18
AS–BR	DA		(I; 2 moles)	Dianisidine	19
AS–GR	NG		(II)	*o*-Toluidine	16, 20, 21
AS–BT; DB			(III)	2,5-Dimethoxyaniline	10
AS–LB	BT		(IV)	*p*-Chloroaniline	16, 20, 22
AS–SG	GB		(V)	*p*-Anisidine	16, 20, 23
AS–SR	RB		(V)	5-Methoxy-*o*-toluidine	16, 20, 23

"NAPHTHOLS" FOR YELLOW SHADES

The "naphthols" derived from BON acid and similar *o*-hydroxycarboxylic acids yield orange, red and deeper colors. The attachment of an arylazo group to a carbon atom in an aliphatic group being one method for preparing yellow dyes, IG in 1921 introduced Naphtol AS–G, which is

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[8] GrE, BP 23,732; DRP 293,897.

[9] Rowe and Levin, *J. Soc. Dyers Colourists* **42**, 207 (1926).

[10] Semard, *Teintex* **4**, 76 (1939).

[11] Rowe, *J. Soc. Dyers Colourists* **46**, 227 (1930).

[12] Rowe and Levin, *ibid.* **40**, 218 (1924).

[13] Ueno and Suzuki, *J. Soc. Chem. Ind.* (*Japan*) **37**, Suppl. binding, 233 (1934).

[14] GrE, BP 13,237; DRP 264,527.

[15] Diserens, The Chemical Technology of Dyeing and Printing, Reinhold, New York, 1948.

[16] Fierz-David, Künstliche Organische Farbstoffe, Ergänzungsband, Springer, Berlin, 1935.

[17] Hopper, MacGregor and Wilson, *J. Soc. Dyers Colourists* **55**, 449 (1939).

[18] IG, FP 818,074.

[19] Rowe and Levin, *J. Soc. Dyers Colourists* **41**, 355 (1925).

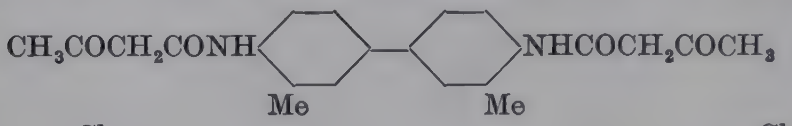
[20] Diserens, *Rev. gén. mat. color.* **40**, 265 (1936).

[21] IG, BP 367,907; DRP 549,983.

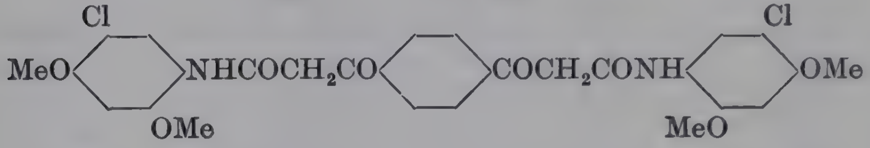
[22] IG, BP 343,164; DRP 551,880.

[23] IG, BP 347,113; DRP 539,116.

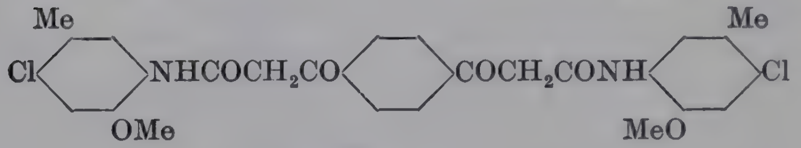
bisacetoacet-*o*-tolidide, as a "naphthol" for yellow shades; coupled on the fiber with diazotized chloroanilines lemon-yellow shades are produced. The poor substantivity and the moderate light fastness of the Naphtol AS–G shades then led to the introduction of Naphtol AS–LG, L3G and L4G; the first two are arylides of terephthaloyl-bis-acetic acid and the third is 2-acetoacetamido-6-ethoxybenzothiazole.[24] With specified diazonium salts the bright yellow shades from Naphtol AS–L4G possess very high light fastness. It is to be noted, however, that because of its adequacy for general purposes, Naphtol AS–G continues to be the commonly used "naphthol" for yellow shades.



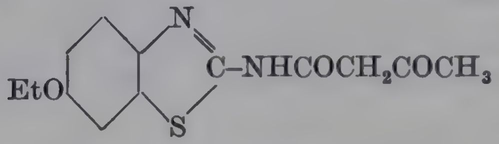
Naphtol AS–G



Naphtol AS–LG



Naphtol AS–L3G



Naphtol AS–L4G

The behavior of Naphtols AS–G, AS–LG and AS–L3G towards diazonium salts is of interest, since these possess two equivalent coupling positions, and their ability to couple with one or two moles of a diazonium salt, and the relative rates of coupling, might have a bearing on the use of the naphthols in dyeing and printing. Under the usual dyeing conditions, a mixture of mono- and disazo dyes is formed. Carrying out the coupling in substance, the disazo dye is readily obtained when two moles of the diazonium salt are used. With one mole of diazonium salt a mixture of monoazo and disazo dye is obtained, the proportion of the latter varying from 40–60%; part of the Naphtol AS–G therefore does not react.[25]

Bradley[26] has found that the azoic dyes from Naphtols AS–LG, AS–L3G and AS–L4G are enolic in structure, since their solutions in pyridine are deepened in color by the addition of methanolic potassium hydroxide. The dyes from Naphtol AS–G are unique in that they are wholly ketonic in form, except when the diazonium salt is from 5-nitro-*o*-anisidine or 5-nitro-*o*-toluidine. The presence of *p*-nitro groups in the two diazonium salts is responsible for the increased acid character of the two dyes.

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[24] Desai and Mehta, *J. Soc. Dyers Colourists* **54**, 422 (1938).

[25] Modak, unpublished work.

[26] *J. Soc. Dyers Colourists* **56**, 298 (1940).

PREPARATION OF NAPHTOLS

Arylamides of BON acid. Naphtol AS and its analogs are prepared by (a) heating a solution of BON acid and the amine in a suitable solvent in the presence of phosphorus trichloride or (b) condensing the previously prepared hydroxynaphthoyl chloride with the base in a suitable solvent. Toluene and chlorobenzene are convenient solvents, and a typical procedure for the first method, which is generally employed in technical practice, is to agitate a mixture of BON acid (1 mole) and amine (1 mole) with toluene (10 times the weight of the amine) at 75–85°, and add phosphorus trichloride (0.4–0.5 mole) in the course of a few hours. The reaction mixture is finally boiled for a few hours, cooled and treated with aqueous sodium carbonate. Toluene is recovered, and the " naphthol " filtered off (yield, about 95%). Further purification is usually not necessary.

The second method may be used in special cases in which the amine does not undergo the acylation by the single stage procedure. The conversion of BON acid into the chloride has to be effected carefully in a solvent to avoid the formation of a depside. A suspension of the acid in benzene or petroleum ether, boiling point 70–80°, may be heated with thionyl chloride until a clear solution results (4–5 hours). The acid chloride separates on cooling and must be used soon after preparation since it decomposes slowly on storage.[2, 27]

The reaction of *o*-hydroxycarboxylic acids with arylamines in presence of phosphorus trichloride or thionyl chloride, as well as the condensation of the preformed acid chlorides with arylamines, results occasionally in mixtures which present problems in separation. In one method suggested for separation, the mixture is neutralized with sodium bicarbonate, and sufficient solvent is allowed to remain to retain tarry material; the amide is filtered off.[28] The use of the amine hydrochloride instead of the free base sometimes gives a smoother reaction and purer products.[29] Benzine, boiling point 110–140°, has been stated to be the best solvent for preparing certain " naphthols,"[30] and ligroin (boiling point 130–135°) to be a better solvent than toluene for the preparation of Naphtol AS–BS.[31]

Acetoacetic arylamides. Naphtol AS–G and the other " naphthols " for yellow shades are prepared by heating the appropriate arylamine with ethyl acetoacetate in molar proportions in a suitable solvent (e.g., xylene). An aluminum kettle may be employed in technical practice. The ethanol formed in the reaction ($CH_3COCH_2COOEt+ArNH_2 \longrightarrow CH_3COCH_2CONHAr$

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[2] See p. 651.

[27] Bhat, Forster and Venkataraman, *ibid.* **56,** 166 (1940).

[28] Weiss, Wintringham and American Cyanamid, USP 2,410,397.

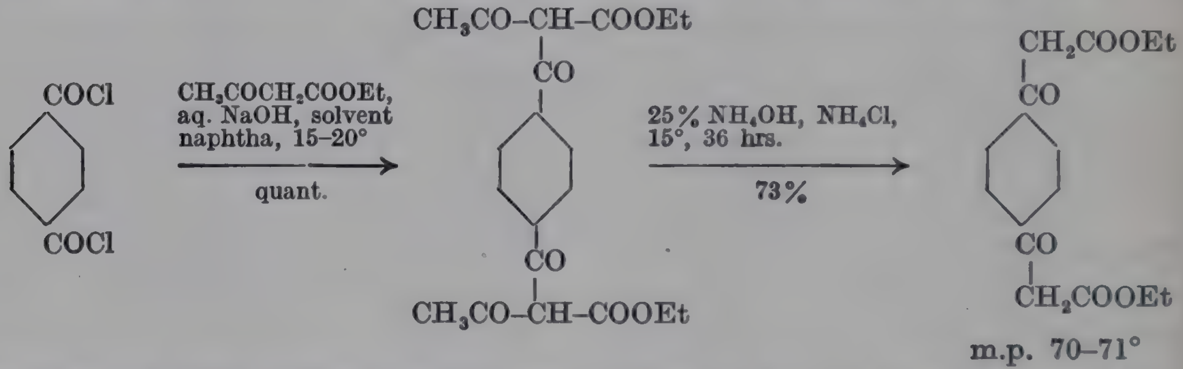
[29] Tinker, Spiegler and du Pont, USP 1,890,201; 1,890,202.

[30] Volkhin, *Anilinokras. Prom.* No. I, **3,** 11 (1933); MLB, DRP 294,799.

[31] Zavel'skiî, *Anilinokras. Prom.* No. I, **3,** 19 (1933); see also Weis, Wintringham and American Cyanamid, USP 2,418,326.

+EtOH) tends to slow it down, and it is best to distil off the ethanol continuously. A small amount of caustic soda, pyridine or triethanolamine (about 2% on the weight of the arylamine) assists the condensation. The reaction is complete in about two hours at the boiling point of the solvent, and on cooling, the "naphthol" crystallizes out (yield 90–95%). Acetoacetanilide and the analogs from *o*-toluidine, *o*-anisidine, *m*-4-xylidine and the chloroanilines, which are important intermediates for yellow azoic pigments, are prepared in a similar manner.[2] Acetoacetanilides can also be prepared from the amines and diketene.[32]

Terephthaloyl-bis-acetic ethyl ester, from which Naphtol AS–LG and L3G are made by condensation with two moles of the appropriate amine, is prepared from terephthaloyl chloride by the usual method.[33] 2-Amino-6-ethoxybenzothiazole, for Naphtol AS–L4G, is prepared[3] from *p*-phenetidine by heating with sodium thiocyanate and monohydrate in chlorobenzene solution at 90°, and cyclizing the thiourea without isolation by means of sulfur chloride at 80°.[3, 34]



HYDROLYTIC FISSION OF THE NAPHTOLS

The constitution of several of the Naphtols was determined by Rowe[11, 19, 35, 36] by hydrolysis with dilute sulfuric acid, boiling point 140–145°, and later[37] by means of 98% sulfuric acid; BON acid and the arylamine were isolated and identified. Sulfuric acid hydrolysis is not very satisfactory; charring occurs with dilute sulfuric acid and the yields are low; with concentrated sulfuric acid the arylamine is sulfonated and dealkylated if it contains an alkoxyl group. Naphtols AS–ITR, AS–LT, AS–LB, AS–SG, AS–SR, AS–LG and AS–L3G have been hydrolysed by heating with 50% aqueous sodium hydroxide at about 200° in an autoclave.[13, 24] During the alkaline hydrolysis of Naphtol AS–LB, the acid is decarboxylated to 2-hydroxycarbazole. In view of the formulation of Naphtol AS–LB in the literature as the *p*-chloroanilide of both 3-hydroxycarbazole-2-carboxylic acid[24, 38] and 2-hydroxycarbazole-3-carboxylic acid,[1, 3] and as the *o*-toluidide of the latter acid,[16] the constitution of the Naphtol has been reexamined.[39] Hydrolysis with 50% aqueous caustic soda at 200° gives *p*-chloroaniline and 2-hydroxycarbazole, identical in melting point, absorption spectra and other properties with a specimen prepared from authentic 2-nitrocarbazole via the amine and the diazonium salt, and different from 3-hydroxycarbazole prepared from 3-chlorocarbazole.

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[2] See p. 651.

[32] Boese, *Ind. Eng. Chem.* **32,** 16 (1940); USP 2,152,132; Williams and Krynitsky, *Org. Syntheses* **21,** 4.

[33] See Chapter III.

[3] See p. 651.

[34] Cf. Allen and Van Allan, *Org. Syntheses* **22,** 16.

[11] See p. 653.

[19] See p. 653.

[35] Rowe and Levin, *J. Soc. Dyers Colourists* **40,** 227 (1924).

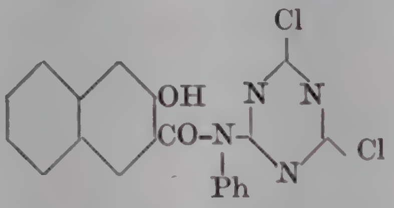
[36] Rowe and Levin, *ibid.* **42,** 82 (1926).

[37] Rowe and Giles, *ibid.* **51,** 287 (1935).

[13] See p. 653.

[24] See p. 654.

Cyanuric chloride reacts with the amide group and not with the hydroxyl in Naphtol AS in faintly alkaline solution; and the product (I) is readily hydrolysed to BON acid by 1% caustic soda solution at 50°. This reaction provides a useful method for the hydrolysis of Naphtols; Naphtol AS–GR for instance gives a 75% yield of 2-anthrol-3-carboxylic acid.[40] Naphtol AS–GR gives a negligible amount of the acid by boiling with 20% alcoholic caustic potash for 48 hours, and with 50% alkali under pressure the product is β-anthrol and not the carboxylic acid. Mono-, di- and triethanolamines and ethylenediamine effect a smooth hydrolysis of the arylamides of hydroxycarboxylic acids into their components without affecting alkoxyl groups in the arylamine residue; but these reagents cannot be used for hydrolysis of the arylamides of acetoacetic, benzoylacetic and terephthaloyl-bis-acetic acids, since the acid components are completely decomposed and are not isolable.[17] Distillation with soda-lime is a convenient method for identifying the arylamine residue in the arylamides of BON acid.[41]



(I)

Naphtol AS–S was marketed by IG in 1938 as a highly substantive naphthol for red combinations.[42] It was recommended for machine dyeing and was stated to answer the repeated demands for Naphtol AS dyeings of superior fastness to rubbing. Combinations of Naphtol AS–S with specified Fast Red Salts (FR, F3G and RL) were regarded as particularly valuable. Hydrolysis of Naphtol AS–S is best carried out by the prolonged action of boiling 16% alcoholic potassium hydroxide.[6]

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[24] See p. 654.

[38] Rowe, The Development of the Chemistry of Commercial Dyes, Institute of Chemistry, London, 1938, p. 34.

[1] See p. 650.

[3] See p. 651.

[16] See p. 653.

[39] Krishna, unpublished work.

[40] Talavdekar, unpublished work.

[17] See p. 653.

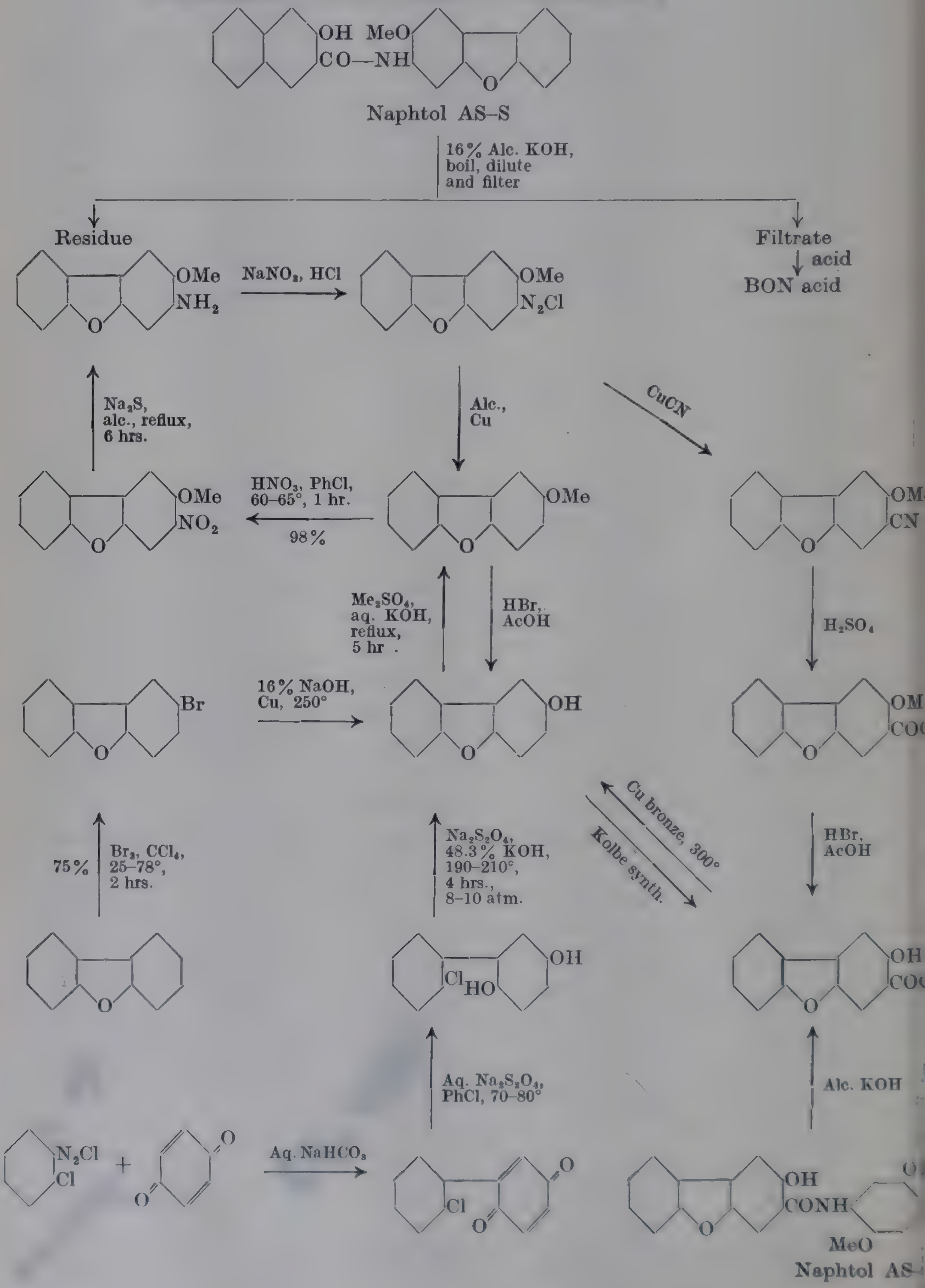
[41] Cross and Carlene, *J. Soc. Dyers Colourists* **59**, 191 (1943).

[42] IG, DRP 508,395; 679,976; 593,506; USP 2,050,958.

[6] See p. 652.

CHART 1

DECOMPOSITION AND SYNTHESIS OF NAPHTOL AS–S


OH MeO
CO—NH
O
Naphtol AS–S
16% Alc. KOH, boil, dilute and filter
Residue
Filtrate
acid
BON acid
OMe
NH₂
O
NaNO₂, HCl
OMe
N₂Cl
O
Na₂S, alc., reflux, 6 hrs.
Alc., Cu
CuCN
OMe
NO₂
O
HNO₃, PhCl, 60–65°, 1 hr.
98%
OMe
O
OM
CN
O
Me₂SO₄, aq. KOH, reflux, 5 hr.
HBr, AcOH
H₂SO₄
Br
O
16% NaOH, Cu, 250°
OH
O
OM
CO
O
75%
Br₂, CCl₄, 25–78°, 2 hrs.
Na₂S₂O₄, 48.3% KOH, 190–210°, 4 hrs., 8–10 atm.
Cu bronze, 300°
Kolbe synth.
HBr, AcOH
O
Cl HO
OH
OH
CO
O
Aq. Na₂S₂O₄, PhCl, 70–80°
Alc. KOH
N₂Cl
Cl
+
O
O
Aq. NaHCO₃
Cl
O
O
OH
CONH
O
O
MeO
Naphtol AS

ESTIMATION OF THE NAPHTOLS

Dyeing, volumetric, gravimetric, colorimetric, and spectrometric methods have been used for estimating the Naphtols, particularly for substantivity determinations. A simple procedure[43] is to acidify the solution of the "naphthol" in aqueous or aqueous-alcoholic caustic soda, and weigh the precipitated "naphthol." This method is adequate for many purposes, but it is sometimes inapplicable for substantivity determinations in which wetting agents are employed, because of difficulties in filtration or in washing the precipitated "naphthol" free from the wetting agent. The usual dyehouse method of examination of a "naphthol" consists of dye-trials in which varying percentages are applied to cotton, developed and soaped under standard conditions, and the azoic shade is matched visually with standard shades from the chemically pure "naphthol." The azoic dye on the fiber may also be estimated in terms of the nitrogen content by a Kjeldahl determination. When an alkaline solution of a "naphthol" is titrated with a diazonium salt solution, the end point is difficult to determine, because of occlusion of uncoupled arylamide by the precipitated azo dye. Various remedies have been suggested, such as the addition of pyridine[44] and alcohol to the "naphthol" solution after neutralizing most of the caustic soda by means of acetic acid. After coupling the "naphthol" with a diazonium salt, such as diazotized sulfanilic acid, the azo dye solution may be estimated colorimetrically,[45, 46] by means of a spectrophotometer or photoelectric absorptiometer using visible light.[47] Uncoupled "naphthol" solutions can be determined directly in a Spekker absorptiometer with ultraviolet illumination, since solutions of the arylamides of BON and similar acids absorb strongly in the ultraviolet.[48]

FAST BASES AND FAST SALTS[3, 4, 33]

Any primary aromatic amine, which is capable of diazotization and coupling and is free from sulfonic and other solubilizing groups, may in principle be used for azoic dyeing; but shade, fastness and other considerations, such as the ability to couple smoothly with "naphthols" on the fiber under the normal conditions of development, have restricted the number of technically used amines to about fifty. The amines recommended for azoic dyeing are marketed as Fast Bases (IG) (Table II), or as Bases with a prefix indicating the trade name for an azoic coupling component.

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[43] Rath, *J. Soc. Dyers Colourists* **44,** 10 (1928); Forster, Mehta and Venkataraman, *ibid.* **54,** 210 (1938).

[44] Mehta and Thosar, *ibid.* **56,** 160 (1940).

[45] Cherkasova, *Zavodskaya Lab.* **9,** No. 1, 116 (1940).

[46] Gürtler, *Melliand Textilber.* **4,** 378 (1923).

[47] Cropper and Giles, *J. Soc. Dyers Colourists* **60,** 279 (1944).

[48] Giles, *ibid.* **61,** 47 (1945).

[3] See p. 651.

[4] See p. 651.

[33] See p. 656.

TABLE II

FAST BASES (IG) AND/OR SALTS

Name	*Constitution*	*Ref.*
Fast Yellow G, GC	*o*-Chloroaniline	12
Fast Orange G, GC	*m*-Chloroaniline	19
Fast Orange GR	*o*-Nitroaniline	11
Fast Orange R	*m*-Nitroaniline	12
Fast Orange RD*, RDA	4-Chloro-3-aminobenzotrifluoride	4
Fast Orange GGD*	5-Amino-1,3-bis-trifluoromethylbenzene	3
Fast Orange LG*	2-Aminodiphenylsulfone	3
Fast Golden Orange GR*	Ethyl 2-amino-4-trifluoromethylphenyl sulfone	4
Fast Scarlet GG	2,5-Dichloroaniline	49
Fast Scarlet TR	6-Chloro-*o*-toluidine	36
Fast Scarlet G, GC	4-Nitro-*o*-toluidine	12
Fast Scarlet RC, R	4-Nitro-*o*-anisidine	12
Fast Scarlet VD	5-Chloro-2-aminobenzotrifluoride	4
Fast Scarlet B	β-Naphthylamine	16
Fast Scarlet LG*	Benzyl 3-amino-4-methoxyphenyl sulfone	10
Fast Red GG Nitrazol C, CF, K extra	*p*-Nitroaniline	4, 16
Fast Red 3GL	4-Chloro-2-nitroaniline	12
Fast Red KB	4-Chloro-*o*-toluidine	19
Fast Red TR	5-Chloro-*o*-toluidine	36
Fast Red RL	5-Nitro-*o*-toluidine	19
Fast Red G, GL	3-Nitro-*p*-toluidine	12
Fast Red AL	α-Aminoanthraquinone	11
Fast Red BB	*o*-Anisidine	12
Fast Red B	5-Nitro-*o*-anisidine	12
Fast Red R, RC	4-Chloro-*o*-anisidine	12
Fast Red ITR	*o*-Anisidine-4-sulfondiethylamide	16
Fast Red RBE	6-Benzamido-*m*-4-xylidine	11
Fast Red FG*	4-Chloro-2-aminodiphenyl oxide	10
Fast Red F3G	4-Chloro-6-cyano-*m*-toluidine	3
Fast Red FR new	4,4′-Dichloro-2-aminodiphenyl oxide	3, 10
Fast Red GTR*	Ethyl 3-amino-4-methoxyphenyl sulfone	10
Fast Bordeaux BD	4-Cyano-2,5-dimethoxyaniline	3
Fast Bordeaux GP	3-Nitro-*p*-anisidine	16
Fast Blue Red O	3-Nitro-*p*-phenetidine	50
Fast Brown RR*	2,6-Dichloro-*p*-phenylenediamine	
Fast Brown V	2-Chloro-4-nitro-2′-amino-4′methoxy-5′-methylazobenzene	3
Fast Garnet B	α-Naphthylamine	12
Fast Garnet GB, GBC	*o*-Aminoazotoluene	12
Fast Garnet GC	*m*-Aminoazotoluene	15
Fast Corinth V*	2-Nitro-4′-amino-5′-methoxy-2′,4-dimethylazobenzene	
Fast Corinth B, R	Benzidine	50
Fast Corinth LB*	4-Chloro-6-benzamido-*m*-anisidine	3
Fast Violet B	6-Benzamido-4-methoxy-*m*-toluidine	16
Variamine Blue RT	*p*-Aminodiphenylamine	16

[3, 4] See p. 651. [10, 11, 12, 15, 16, 19] See p. 653. [36] See p. 656.

[49] Rowe and Corbishley, *ibid.* **41**, 278 (1925).

[50] Dorman, *Am. Dyestuff Reptr.* **28**, 82, 83 (1939).

TABLE II (*continued*)

Name	*Constitution*	*Ref.*
Variamine Blue B	4-Amino-4′-methoxydiphenylamine	11
Variamine Blue FG	4-Amino-3-methoxydiphenylamine	4
Fast Blue B	Dianisidine	16, 49
Fast Dark Blue R*	(formerly *o*-Tolidine) 2,6-dichloro-4-nitro-4′-amino-2′,5′-dimethoxyazobenzene	
Fast Blue RR	4-Benzamido-2,5-dimethoxyaniline	16
Fast Blue BB	4-Benzamido-2,5-diethoxyaniline	16
Fast Black LB	4-(*o*-Ethoxy)benzeneazo-1-naphthylamine	12
Fast Black B	4,4′-Diaminodiphenylamine	3, 50
Fast Black G*	4′-Amino-5′-ethoxy-4-(*p*-aminophenylamino)-2′-methylazobenzene	4
Fast Black K*	4-Nitro-4′-amino-2′,5′-dimethoxyazobenzene	

The work of the dyer has been facilitated by the production of diazonium salts in stabilized form (Fast Salts), which have merely to be dissolved in water and used (see Chapter IV). Although it is therefore no longer necessary in azoic dyeing practice for diazotization to be carried out, there are cost and (in special cases such as package dyeing in machines) other factors to be considered, as a result of which dyehouses still frequently prefer to purchase the Fast Bases and diazotize them as required. One advantage in this procedure is the high purity in which the Fast Bases are available, so that the dyer is aware of the precise composition of his diazonium solution. It will be noticed from Table II that, while most of the Fast Bases are also commercially available as Salts, some are marketed only in the latter form in view of the special methods of diazotization which the dyer cannot conveniently perform.

The Fast Bases marked * are stabilized as the zinc chloride compounds of the diazonium salts, when they are marketed as Fast Salts. The stabilizing agents used for certain other Fast Salts are given in Table III.

TABLE III

Stabilizing Agents for Fast Salts[51]

Fast salt	*Stabilizing agent*
Nitrazol CF extra	Fluoboric acid
Nitrazol CFK extra	Chlorobenzene-4-sulfonic acid
Orange RDA	Naphthalene-1,5-disulfonic acid
Scarlet VD	Naphthalene-1,5-disulfonic acid
Red F3G	Nitrobenzene-*m*-sulfonic acid or Benzenesulfonic acid
Red FR new	Cobaltous chloride
Red FRK	Ethylsulfuric acid
Garnet GBC	Sulfuric acid ; Glauber salt

[3, 4] See p. 651.

[11, 12, 16] See p. 653.

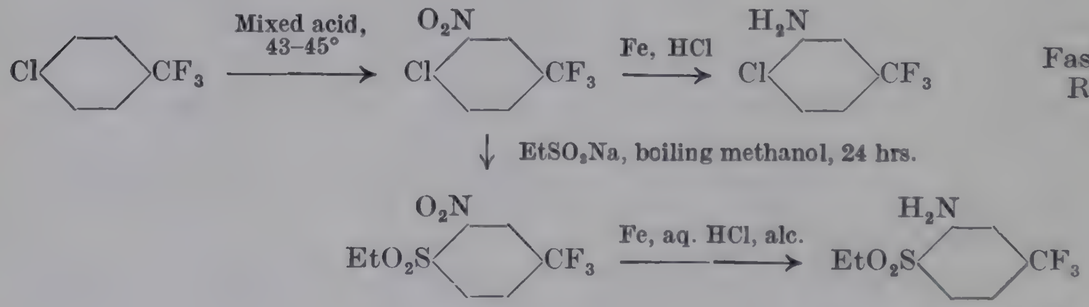
[49, 50] See p. 660.

[51] *BIOS* 988.

Other dyestuff manufacturers market a parallel but more limited range of amines and stabilized diazonium salts for use in azoic dyeing. Some of the Ciba Bases are constituted as follows: 2′,4-dichloro-2-aminodiphenyl oxide (Scarlet Ciba IV Base); 4-amino-3-methoxyazobenzene (Bordeaux Ciba III Base); 5-(*p*-chloro)benzeneazo-4-ethyl-*o*-anisidine (Violet Ciba I Base);[15] *p*-aminobenzeneazo-1-naphthalene (Violet Ciba II Base);[15] 4-*p*-tolyloxyacetamido-2,5-dimethoxyaniline (Violet Ciba III Base). 2-Chloro-*p*-anisidine (Scarlet Base N3J); 2-nitro-*m*-4-xylidine (Rouge Base NK); and 2-nitro-5-methoxy-*p*-toluidine (Rouge Base NCL) are Ku products.[10, 15]

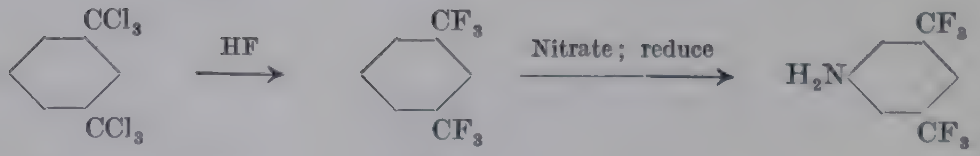
While some of the Fast Bases are made in the normal course of dye manufacture as intermediates[33] for azo and other dyes, several are of interest solely or primarily as Fast Bases and Salts. The preparation of some of the Fast Bases[2, 3, 4] involves a long series of reactions which the dye manufacturer undertakes for filling gaps in the color scale of the azoic dyes, notwithstanding the meager demand for such a base.

Fluorine compounds. Among the Fast Bases are four compounds containing the trifluoromethyl group, which unlike the trichloromethyl group is remarkably stable to hydrolysis. They are prepared by the indicated series of reactions, starting from the appropriate benzotrifluoride derivative.[33] When these bases are employed in azoic dyeing, the influence of the trifluoromethyl group is to improve the clarity of the tone and the light fastness, but to reduce washing fastness.

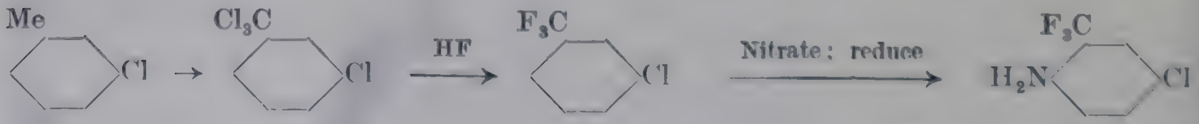

Cl
CF$_3$
Mixed acid, 43–45°
O$_2$N
Cl
CF$_3$
Fe, HCl
H$_2$N
Cl
CF$_3$
EtSO$_2$Na, boiling methanol, 24 hrs.
O$_2$N
EtO$_2$S
CF$_3$
Fe, aq. HCl, alc.
H$_2$N
EtO$_2$S
CF$_3$

Fast Orange RD Base

Fast Golden Orange GR Base


CCl$_3$
CCl$_3$
HF
CF$_3$
CF$_3$
Nitrate; reduce
H$_2$N
CF$_3$
CF$_3$

Fast Orange GGD Base


Me
Cl
Cl$_3$C
Cl
HF
F$_3$C
Cl
Nitrate; reduce
F$_3$C
H$_2$N
Cl

Fast Scarlet VD Base

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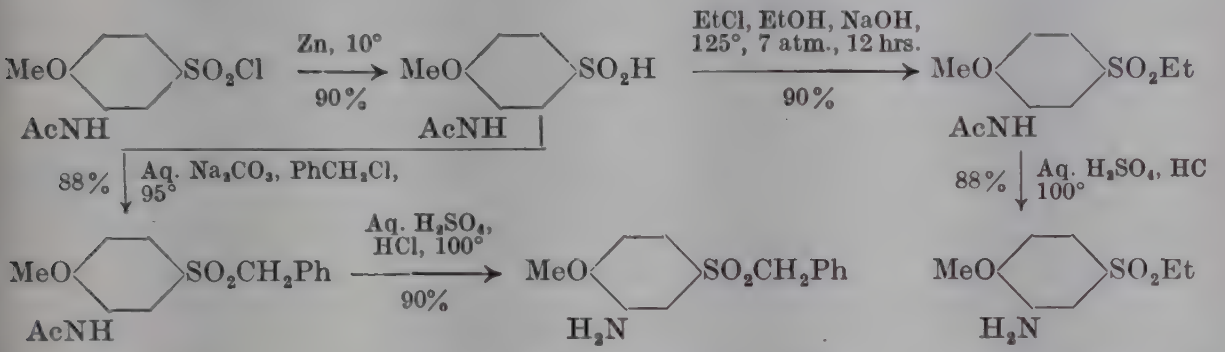
[15] See p. 653.
[10] See p. 653.
[33] See p. 656.
[2, 3, 4] See p. 651.

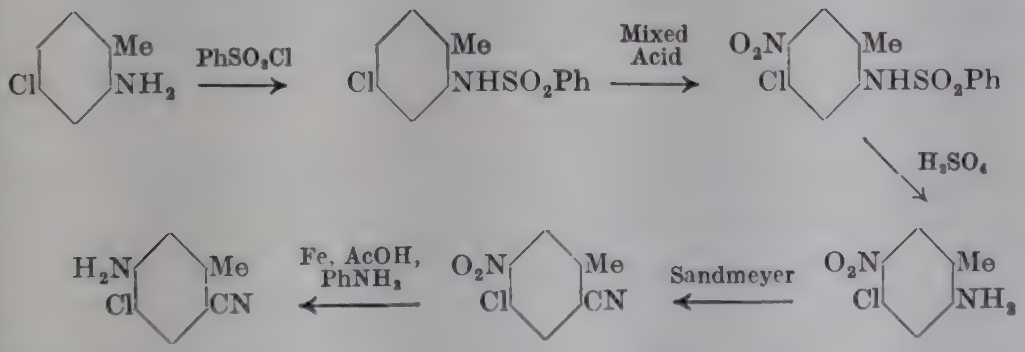
Sulfones. Azoic shades of good light fastness are obtained from Fast Bases containing a sulfone group. Fast Orange LG Base is *o*-aminodiphenylsulfone, prepared[2] by heating *o*-dinitrobenzene with benzenesulfinic acid (which must be used immediately after preparation since it is unstable) at 130–135° in an autoclave for 15 hours; *o*-nitrodiphenylsulfone thus obtained is then reduced. Acet-*o*-anisidide is the starting point for several Fast Bases:[3] Scarlet LG, Red GTR and Red ITR.


MeO
SO₂Cl
AcNH
Zn, 10°
90%
MeO
SO₂H
AcNH
EtCl, EtOH, NaOH, 125°, 7 atm., 12 hrs.
90%
MeO
SO₂Et
AcNH
88%
Aq. Na₂CO₃, PhCH₂Cl, 95°
88%
Aq. H₂SO₄, HC 100°
MeO
SO₂CH₂Ph
AcNH
Aq. H₂SO₄, HCl, 100°
90%
MeO
SO₂CH₂Ph
H₂N
MeO
SO₂Et
H₂N

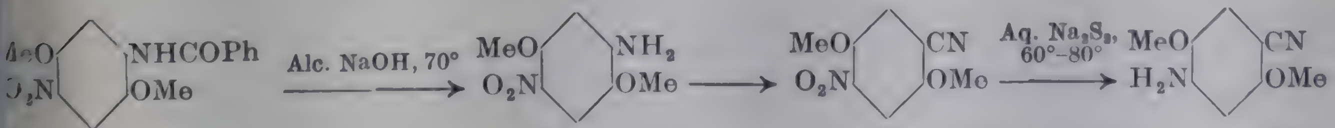
Fast Scarlet LG Base

Fast Red GTR Base

Nitriles. Fast Red F3G and Fast Bordeaux BD Base are unique among the Fast Bases in containing a nitrile group; IG made them only in small quantities.[2] Fast Bordeaux BD Base utilizes an intermediate for Fast Blue RR Base.[3]


Me
NH₂
Cl
PhSO₂Cl
Me
NHSO₂Ph
Cl
Mixed Acid
O₂N
Me
Cl
NHSO₂Ph
H₂SO₄
H₂N
Me
Cl
CN
Fe, AcOH, PhNH₂
O₂N
Me
Cl
CN
Sandmeyer
O₂N
Me
Cl
NH₂

Fast Red F3G Base


MeO
NHCOPh
O₂N
OMe
Alc. NaOH, 70°
MeO
NH₂
O₂N
OMe
MeO
CN
O₂N
OMe
Aq. Na₂S₂, 60°–80°
MeO
CN
H₂N
OMe

Fast Bordeaux BD Base

Blue Bases. The few Bases available for the production of blue shades (and of dark green shades in combination with Naphtol AS-GR) are derivatives of diphenylamine or aminohydroquinone ethers. Variamine

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[2] See p. 651.

[3] See p. 651.

Blue B and FG are isomeric compounds, prepared by two different series of reactions.[2] Variamine Blue FG is marketed only as the stabilized diazonium salt.

CHART 2

PREPARATION OF VARIAMINE BLUE B

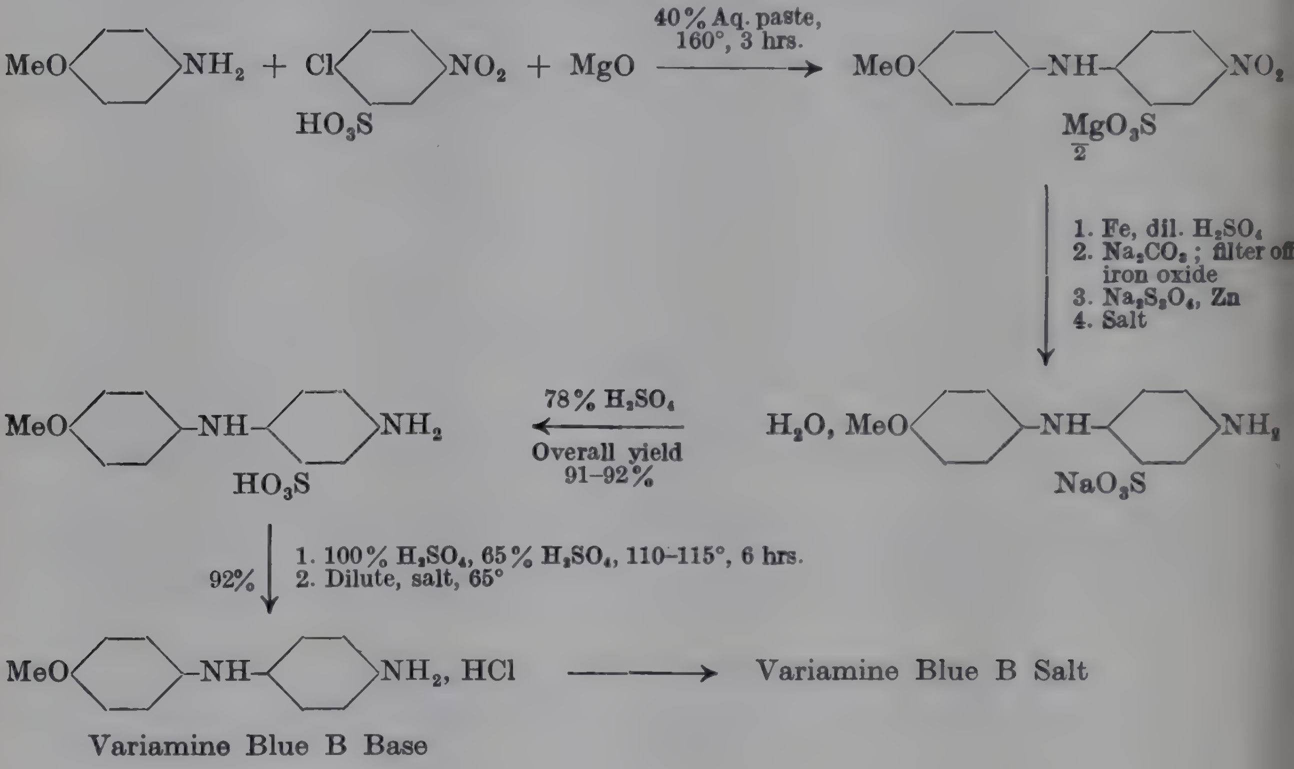
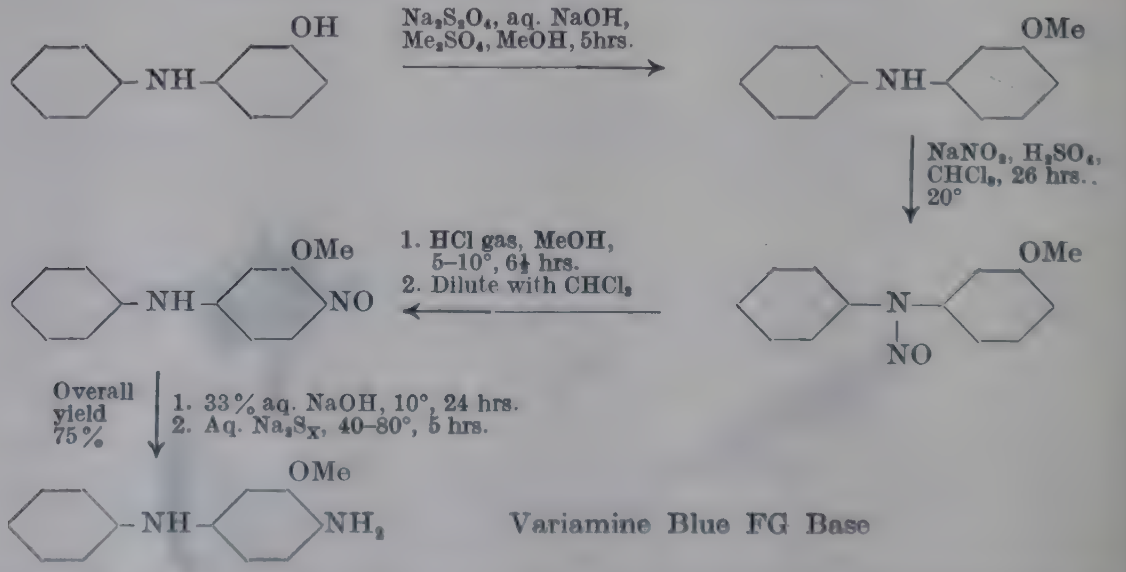

MeO
NH₂
Cl
NO₂
HO₃S
MgO
40% Aq. paste, 160°, 3 hrs.
MeO
NH
NO₂
MgO₃S / 2
1. Fe, dil. H₂SO₄
2. Na₂CO₃; filter off iron oxide
3. Na₂S₂O₄, Zn
4. Salt
H₂O, MeO
NH
NH₂
NaO₃S
78% H₂SO₄
Overall yield 91–92%
MeO
NH
NH₂
HO₃S
92%
1. 100% H₂SO₄, 65% H₂SO₄, 110–115°, 6 hrs.
2. Dilute, salt, 65°
MeO
NH
NH₂, HCl
Variamine Blue B Salt
Variamine Blue B Base

CHART 3

PREPARATION OF VARIAMINE BLUE FG BASE


NH
OH
Na₂S₂O₄, aq. NaOH, Me₂SO₄, MeOH, 5hrs.
NH
OMe
NaNO₂, H₂SO₄, CHCl₃, 26 hrs., 20°
N
NO
OMe
1. HCl gas, MeOH, 5–10°, 6½ hrs.
2. Dilute with CHCl₃
NH
OMe
NO
Overall yield 75%
1. 33% aq. NaOH, 10°, 24 hrs.
2. Aq. Na₂Sₓ, 40–80°, 5 hrs.
OMe
NH
NH₂
Variamine Blue FG Base

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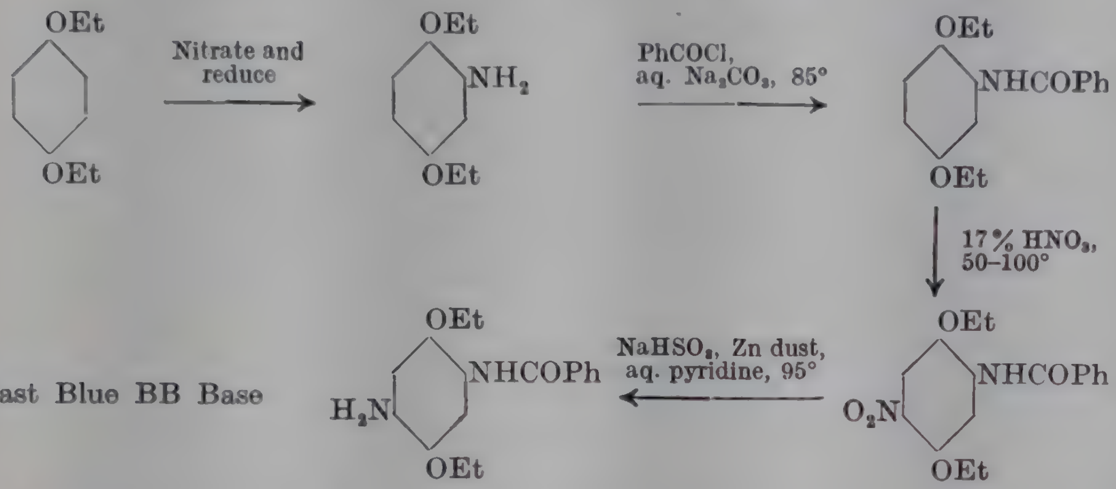
[2] See p. 651.

Fast Blue BB and RR Bases, the latter being the dimethoxy analog, are made by a similar series of reactions, starting with the appropriate ether of hydroquinone.

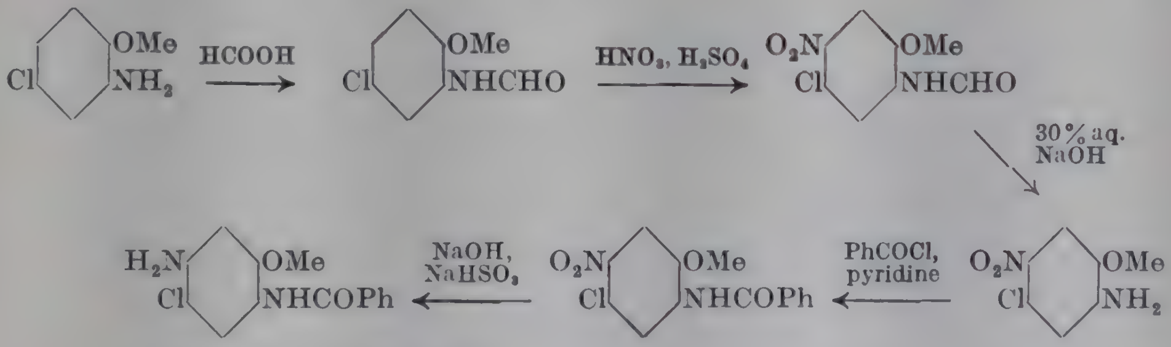
CHART 4

PREPARATION OF FAST BLUE BB BASE


OEt
OEt
Nitrate and reduce
NH$_2$
PhCOCl, aq. Na$_2$CO$_3$, 85°
NHCOPh
17% HNO$_3$, 50–100°
O$_2$N
NaHSO$_3$, Zn dust, aq. pyridine, 95°
H$_2$N

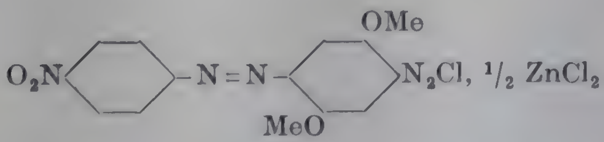
Fast Blue BB Base

Fast Corinth LB Base is prepared from 4-chloro-*o*-anisidine. An interesting feature of the process is the reduction of the nitro compound in pyridine solution, without isolation after the benzoylation stage, by means of caustic soda solution and sodium bisulfite at 100°.[3]


OMe
NH$_2$
Cl
HCOOH
NHCHO
HNO$_3$, H$_2$SO$_4$
O$_2$N
30% aq. NaOH
PhCOCl, pyridine
NHCOPh
NaOH, NaHSO$_3$
H$_2$N

Fast Corinth LB Base

Fast Black Salts G and K are typical of diazonium components for azoic dyeing which are marketed only as stabilized salts, and not as the amines. The preparation of Black G Salt, which leads to a trisazo dye on the fiber, is appended. After mixing with Glauber salt and zinc sulfate, the product is dried at 40–45°, and standardized at 20.5%.



$\mathrm{O_2N{-}C_6H_4{-}N{=}N{-}C_6H_2(OMe)(MeO){-}N_2Cl,\ {}^1/_2\,ZnCl_2}$

Fast Black K Salt

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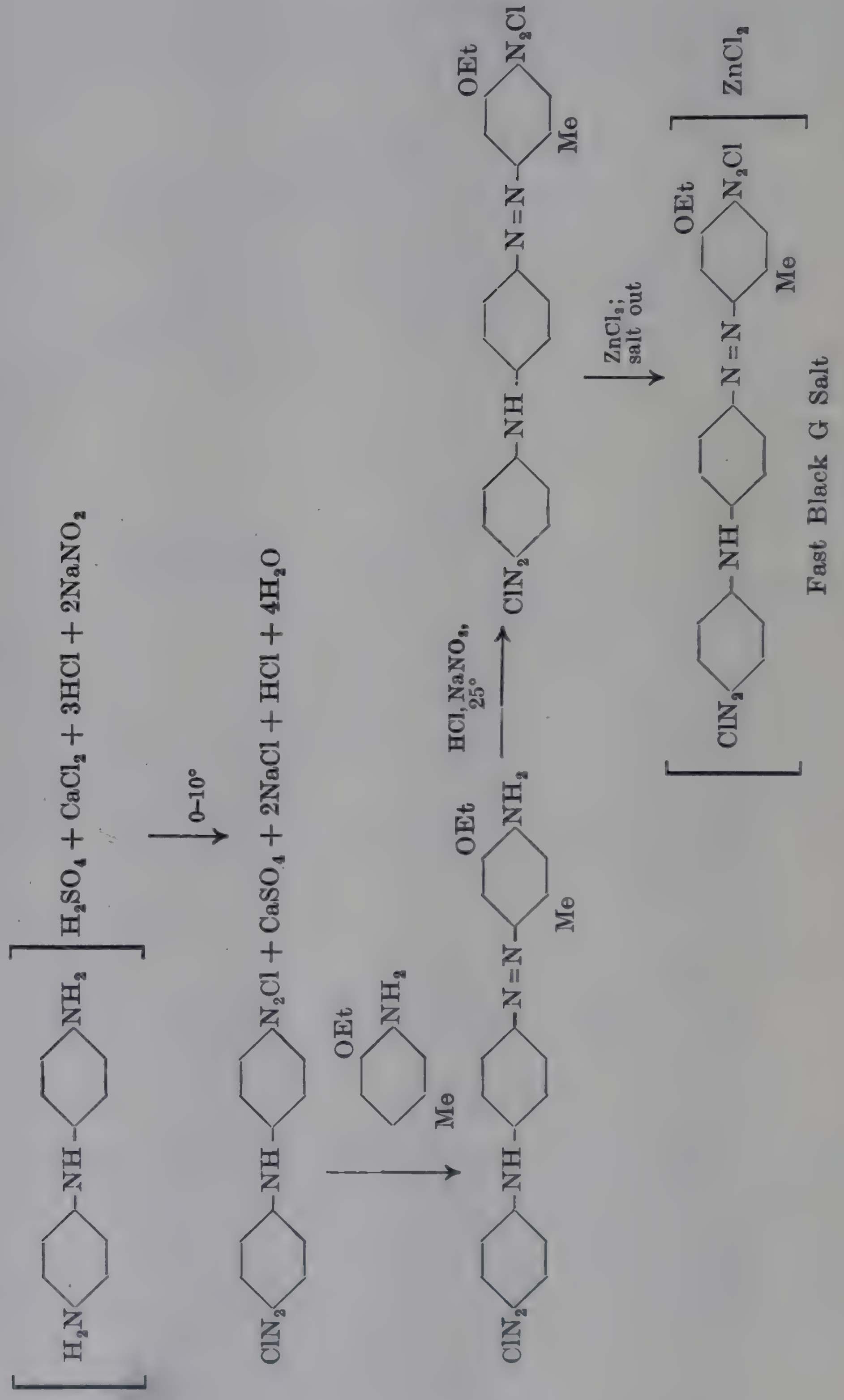
[3] See p. 651.

CHART 5

PREPARATION OF FAST BLACK G SALT


H₂N
NH
NH₂
H₂SO₄ + CaCl₂ + 3HCl + 2NaNO₂
0–10°
ClN₂
NH
N₂Cl + CaSO₄ + 2NaCl + HCl + 4H₂O
OEt
NH₂
Me
ClN₂
NH
N=N
OEt
NH₂
Me
HCl, NaNO₂, 25°
ClN₂
NH
N=N
OEt
N₂Cl
Me
ZnCl₂; salt out
ClN₂
NH
N=N
OEt
N₂Cl
Me
ZnCl₂
Fast Black G Salt

AZOIC SHADES

Unlike other groups of dyes in which the name of the dye (Congo Red; Caledon Jade Green; Diamine Sky Blue) immediately indicates the shade produced on textiles, the names of "naphthols" and Fast Bases are somewhat confusing. The Naphtol or Brenthol gives no indication of the colors of the dyes derived from it, for the reason that a given "naphthol" can lead to a variety of shades. However, for many of the Naphtols the letters following AS are pointers to the character of the shades for which the Naphtols are specially intended (TR, turkey red; ITR, turkey red of Indanthrene fastness; G, gelb = yellow; L4G, yellow with high light fastness; GR, green; SG, schwartz-grün = greenish black; SR, reddish black). Some Brenthol names are related to the constitution (AT = acetoacet-tolidide; BN = β-naphthalide; AN = α-naphthalide). The names of the Bases and Salts sound more specific, but actually they are not, except to the extent that the names represent the typical or staple shades for which the Bases and Salts are intended to be used. Thus bordeaux shades are commonly produced from Bordeaux GP and Naphtol AS, AS–SW, etc., but Bordeaux GP also gives a useful yellow shade in combination with Naphtol AS–G.

The Naphtols may be divided into two broad classes on the basis of the azoic shades: (1) Naphtols which yield a series of shades according to the diazonium salt used for development as indicated by the name of the Base or Salt (Scarlet, Orange, Red, Blue, Black); and (2) speciality Naphtols, which are so constituted that each yields more or less the same shade with any Base or Salt; such Naphtols are AS–G (yellow to yellow-brown); LB (various tones of brown, except with Black Salts which give black shades); SG and SR (black); Naphtol AS–GR is used specifically for producing greens in combination with Blue Bases and Salts.

Table IV lists some technically important azoic combinations for specified shades. Azoic dyes are in general valuable for medium and full shades, and are not used for pale shades, which exhibit markedly inferior light fastness.

TABLE IV

Technically Important Azoic Combinations for Specific Shades and their Light and Chlorine Fastness

Naphtol	*Base*	*Shade*	*Fastness*	
			Light	*Chlorine*
AS–G	Scarlet GG	Greenish yellow	5–6	3–4
AS–G	Red B	Orange yellow	4–5	4–5
AS–L4G	Red KB	Yellow	6	4
AS	Orange GC	Orange	4–5	4
AS–RL	Orange RD	Orange	6	4–5
AS	Scarlet GG	Scarlet	6	5
AS–SW	Scarlet TR	Scarlet	5–6	4–5
AS–OL	Scarlet GG	Scarlet	6–7	5
AS–BS	Scarlet R	Bluish scarlet	4	5
AS–OL	Red AL	Yellowish red	7	5
AS	Red 3GL	Red	6	4–5
AS–SW	Red KB	Red	5	5
AS–TR	Red TR	Red	5	5

TABLE IV (*continued*)

Naphtol	*Base*	*Shade*	*Fastness* *Light*	 *Chlorine*
AS–ITR	Red ITR	Red	7	5
AS–RL	Red GL	Red	6–7	4–5
AS–BO	Red B	Claret	6–7	4–5
AS–S	Bordeaux BD	Bordeaux	5	5
AS–SW	Bordeaux GP	Bluish bordeaux	6–7	4–5
AS–LT	Corinth LB	Corinth	6–7	4
AS	Violet B	Red violet	5	4–5
AS–TR	Violet B	Red violet	5	4–5
AS	Blue BB	Blue	5–6	4
AS	Blue RR	Reddish blue	5–6	4
AS–D	Blue BB	Blue	5–6	4
AS–LT	Variamine Blue B	Blue	6–7	2
AS–GR	Blue BB	Dark green	4–5	3
AS–GR	Variamine Blue B	Dark green	4	3–4
AS–GR	Variamine Blue FG	Dark green	4–5	2
AS–LB	Orange GC	Khaki	7	4–5
	Red RL	Red brown	7	4
	Red B	Chocolate brown	7	3–4
AS–SG+ AS–SR	Red B	Black	7–8	4
AS–SW	Black G	Black	3–4	3–4

AZOIC DYEING

Azoic dyes are used primarily on cotton and viscose. The dyeing of cotton by means of azoic colors differs radically from the processes of dyeing with direct, basic, sulfur and vat colors, since it is not the dye but an intermediate which is absorbed from solution, and the dye is formed on the fiber by the interaction of two components. As a consequence, and in view of the variety of "naphthols" and bases, azoic dyeing is relatively complicated, and for the application of the azoic colors to the fullest advantage, the dyer has to be aware of the many factors involved in the three stages of naphtholation, coupling and aftertreatment. The fastness of azoic dyed materials to light, rubbing and other agencies is dependent on the constitution of the dyes, but the maximum fastness possible for a given combination can only be obtained by adopting the right methods of dyeing.

Impregnation of the fiber with alkali naphtholate ("naphtholation"). The "naphthol" is dissolved by pasting it with a good wetting and emulsifying agent, such as a fatty alcohol sulfate or sulfonated castor oil, adding caustic soda solution and boiling water, and further heating if necessary to get a clear solution. An alternative "cold process" may also be employed in which the "naphthols" are dissolved at room temperature in aqueous caustic soda with the aid of alcohol or methylated spirit;

it is necessary to remember that alcohol reduces the substantivity of the "naphthol." Difficulties arising from the ready hydrolysis and oxidation of the alkali naphtholate on the fiber are avoided by adding formalin. This addition is not made in piece dyeing on a padding machine, where the fabric is impregnated at about 95–100° and dried. Formaldehyde is only added if the damp material is allowed to lie for some time. The addition of formaldehyde to an alkaline "naphthol" solution increases the colloidal character and stabilizes the bath, which can then be allowed to stand for a relatively long time without precipitation. Brass and Sommer[52] have found that formaldehyde condenses with Naphtol AS, AS–BO and AS–SW to form 1,1′-dinaphthylmethane derivatives, the methylene bridge being broken during diazonium coupling; but the reactions need to be investigated more fully.[53] The formation of the methylol under alkaline conditions and its conversion into the dinaphthylmethane on acidification are more probable.[54] Part of the function of formaldehyde is merely to provide a blanket of vapor which prevents the access of atmospheric carbon dioxide and oxygen to the naphtholated yarn.

Several of the "naphthols" do not require the addition of formaldehyde to the impregnation baths, since the stability is adequate in the absence of formaldehyde. Further, the acetoacetarylides (e.g., Naphtol AS–G) form complex condensation products with formaldehyde and lose their ability to couple with diazonium salts, and the reactivity of the "naphthols" in alkaline solution with formaldehyde must therefore be examined before the reagent is used.

The conditions for bringing the "naphthols," especially those of high molecular weight, into solution have to be studied by the dyer; if he considers that elimination of the process justifies the increased cost, he can turn to the "Solunaphtols,"[55] which contain a suitable alkali and a wetting agent, so that the "naphthol" bath is prepared merely by adding hot water. Solunaphtols (J. W. Leitch and Co.) have good penetrating power and the solutions have comparatively high resistance to hard water, since the "naphthols" are maintained in a highly dispersed state in the presence of fixed alkali with the aid of suitable surface-active agents.

The application of "naphthols" to cotton material (yarn and cloth) calls for careful manipulation. On yarn they are mostly applied by "tub-liquoring," which consists in impregnating the yarn by hand for about thirty seconds in the alkaline solution of the "naphthol" (the concentration depending on the affinity of the "naphthol" and the strength of the required azoic shade), squeezing and hydroextracting. The quantity of "naphthol" taken up by the yarn is calculated on the basis of its affinity, and the strength of the bath is kept up by adding a feeding bath of the "naphthol" solution of the requisite concentration. Cloth is padded and dried in a hot chamber (hot flue) or over drying cylinders.

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[52] *Ber.* **61,** 993 (1928).

[53] Forster, Ramachandran and Venkataraman, *J. Soc. Dyers Colourists* **54,** 216 (1938).

[54] Cf. Dumas, *Rev. gen. mat. color.* **41,** 449 (1937).

[55] Wallwork, *J. Soc. Dyers Colourists* **55,** 477 (1939).

The absorption of the "naphthols," like the azo direct cotton dyes, is greatly increased by the addition of sodium chloride or sulfate. This is in fact essential for an unsubstantive "naphthol" such as AS–G; and in other cases common salt is added when the naphtholation is carried out in a package dyeing machine, so that the bath may be exhausted.

Development. The naphtholated material is treated with a diazonium salt solution, the mineral acidity of which has been neutralized, usually by the addition of sodium acetate. Yarn is not dried before development, and salt may be added to prevent the diffusion of the sodium naphtholate from the fiber into the developing bath. The presence of a substance with protective colloidal and dispersing properties is an aid to improved fastness to crocking; unfixed pigment is maintained in colloidal solution and its deposition on the fiber is prevented. Diazopon A (IG) and similar products are employed for this purpose. Diazopon A is a 20% solution of Emulphor O, which is a condensate of sperm oil with 20–25 moles of ethylene oxide at 160° in the presence of aqueous caustic soda.[56] The function of substances like Diazopon A during development can be demonstrated by adding a diazonium salt solution to an alkaline solution of β-naphthol or Naphtol AS in the presence or absence of Diazopon A, and filtering the mixture; with Diazopon A a colloidal red solution runs through the filter; and in its absence a precipitate and a clear, practically colorless filtrate are obtained.

An alkali-binding agent is employed during development to neutralize the caustic soda transferred from the fiber.[57] The particular reagent employed is an important factor influencing the final result. It must be inert to the other chemicals which are present, must form no precipitate with caustic soda, and its acidity must correspond to the coupling energy of the diazonium salt. Bases which couple very readily require correspondingly strong acid-reacting compounds, while those with low coupling energy must be coupled in neutral solution. Acetic acid is generally suitable, but aluminum sulfate is sometimes employed for rapid coupling salts. For diazonium salts with low coupling energy (e.g., Variamine Blue and Blue BB), sodium acetate is added in excess. An interesting method of neutralizing excess caustic soda, recommended for special purposes, is to add ammonium chloride and formaldehyde to the diazonium solution, when hexamethylenetetramine is formed and the liberated hydrochloric acid is the effective agent.[58] For Variamine Blue, which is useful for piece dyeing, a " soda developing process " has been suggested. The naphthol-padded and dried cloth is passed through the diazonium solution containing much acetic acid which neutralizes the alkali, but coupling will not take place at this stage. This is effected by subsequent passage through a soda bath, when neutralization of the acetic acid results in immediate coupling. The complete coupling of diazonium salts with extremely low coupling energy is thus ensured. The acetic acid solution of the diazonium salt is stable and it is so well absorbed that there is no difficulty in obtaining level shades with the heaviest cotton materials. Since the coupling in the soda bath is quite rapid, development can be carried out as a continuous process. The presence of triethanolamine sulfate and the condensation product of oleyl alcohol and ethylene oxide facilitates coupling with diazonium salts sensitive to alkali, such as Variamine Blue and Blue BB salts.[59]

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[56] *BIOS* **421,** **518.**

[57] Christ, *Melliand Textilber.* **11,** 447 (1930).

The speed of coupling of a given " naphthol " and diazonium salt depends on the character of both.[60] For the practical purpose of the development of " naphthols " on the fiber, the Naphtols and the Fast Salts may be roughly divided into the following groups, in which (1) represents the lowest and (4) the highest speed of coupling. A Naphtol from group (1) will couple very slowly with a diazonium salt from group (1). A Naphtol from group (4) will couple with a diazonium salt from group (4) very rapidly. *Naphtols:* (1) AS–SG; AS–SR. (2) AS–LT; AS–LB; AS–GR. (3) AS; AS–D; AS–OL; AS–RL; AS–BG; AS–BS; AS–E; AS–TR; AS–ITR; AS–LC; AS–BO; AS–SW; AS–BR. (4) AS–G. *Fast Salts:* (1) Red AL; Red RBE; Corinth LB; Blue BB; Variamine Blue B, FG and RT; Black B; Black K. (1–2) Blue RR; Violet B. (2) Scarlet TR; Red KB; Red TR; Corinth V; Blue B; Black G. (3) Yellow GC; Orange GC; Scarlet GG; Red RC. (4) Orange GR; Orange R; Scarlet G; Scarlet R; Red B; Red GG; Red GL; Red 3GL; Red RL; Bordeaux GP.

Aftertreatment. The development of the material is followed by a thorough wash in cold water and a vigorous soap boil to remove the loosely adhering pigment and produce the maximum fastness obtainable for the particular azoic dye. The marked improvement in fastness properties of azoic dyeings on cotton effected by soaping is well known. Some of the dyeings, which at first are relatively fugitive to light and washing and loose to rubbing, thus acquire good all-round fastness. In general, the fastness, and more particularly the fastness to rubbing, bears a direct relationship to the efficiency of the aftertreatment; and the synthetic detergents and emulsifying agents may be employed with advantage in addition to soap.[53] There is naturally a limit to such improvement, partly because the optimum stage of aggregation of the dye is different for good fastness to rubbing and for good fastness to light. Bean and Rowe[61] have stated: "the object should be to remove loose surface pigment and to produce the first stage of aggregation within the cell wall, but to limit subsequent growth of the pigment particles and their migration as far as possible. This results in increased fastness to light, but with the minimum decrease in fastness to rubbing."

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[58] Jäger, *ibid.* **14,** 401 (1933).

[59] IG, BP 489,972.

[60] See Chapter XI.

Application of azoic dyes to fibers other than cotton.—Viscose. Azoic dyes are useful for fast shades on viscose. The method of application is similar to cotton dyeing, except that the usual precautions have to be taken for preventing mechanical damage to the delicate fiber. Wringing and padding processes are avoided; utilizing salt, both in the "naphtholating" and developing baths, as well as the much greater affinity of viscose for dyes in comparison with cotton, the baths are completely exhausted. Stabilized diazonium salts and alkali-binding agents must be used after examination to ensure that precipitates are not deposited on the fiber, which will diminish the luster of the rayon. Rapid coupling combinations are employed as far as possible. It has been claimed that azoic dyes on viscose are faster to rubbing than they are on cotton. Viscose is "blinded" when certain azoic shades are soaped, and Rowe has shown by microphotographs that the blinded fibers consist of a suspension of microcrystalline aggregates of the coloring matter distributed evenly throughout the colorless fiber.[62] The coagulation or crystallization of the coloring matter within the fibers is solely a temperature effect. The lustrous non-blinded fibers consist of a true solution of the dye in hydrated cellulose.

The influence of the colloidal character of "naphthol" baths on level dyeing is illustrated by the careful control of conditions suggested for applying "naphthols" to viscose cakes in package dyeing machines.[63] A solution of Fixanol (ICI) (a cetylpyridinium salt) is first circulated through the viscose, then the "naphthol" solution in aqueous cellosolve and caustic soda, and finally Calsolene Oil HS (ICI) (sulfonated methyl oleate) and aqueous ammonia; the cakes are then washed with salt solution and developed.

Cellulose acetate. Azoic dyeing has a limited use on acetate rayon for shades requiring higher fastness to boiling and degumming than is obtainable from azoic and anthraquinone dyes used as aqueous dispersions. The ordinary method of "naphtholation" and development described for cotton and viscose is not applicable to acetate rayon, unless it has been saponified. Rohling has shown[64] that, by a variation of the procedure used for cotton, azoic dyeing can be successfully carried out on cellulose acetate with only negligible saponification. Examples have been given of dyeing with Naphtol AS–G, AS–OL, AS–LT and AS–LB and various bases by first mixing the Naphtol and base with ethylene glycol, caustic soda and soft water, pouring the resulting mixture into a bath at 60–65° containing caustic soda, wetting agent, glue, sodium sulfate and sodium nitrite, entering the acetate rayon, waiting an hour, acidifying with formic acid, and after 15 minutes soaping and finishing as usual.[55]

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[53] See p. 669.

[61] *J. Soc. Dyers Colourists* **45**, 67 (1929).

[62] *Ibid.* **42**, 207 (1926).

[63] Courtaulds, Cluley and Taylor, BP 542,779.

Wool and Silk. Since acid, acid-mordant and other groups of dyes provide a full range of fast shades for the animal fibers, azoic dyes are hardly ever used, especially on wool. There are two difficulties in the application of azoic dyes to wool and silk: the sensitivity of both the fibers to alkali and the ability of the fibers themselves to couple with diazonium salts. The latter reaction is hindered by adding acetic acid to the developing bath. Everest and Wallwork[65] have described a method in which caustic soda is avoided in the naphtholating bath. The Naphtols have adequate substantivity for wool if they are applied as aqueous dispersions containing soap and soda ash; for silk, which has much less affinity for Naphtols, salt is used for promoting absorption.

SUBSTANTIVITY OF THE NAPHTOLS

An important feature of Naphtol AS and its analogs is their much greater substantivity in comparison with β-naphthol in alkaline solution; substantivity in this Chapter refers to cotton. Naphtol AS itself has the lowest substantivity among the various members of the series. While the increased substantivity of the Naphtols as a class is a useful property, there are wide variations in the affinity of individual Naphtols, and the value of a " naphthol " cannot be reckoned solely in terms of its substantivity. Thus Naphtol AS and Naphtol AS–BS, possessing low and moderate substantivity, are widely used. Naphtol AS–BR is highly substantive, but the azoic shades are of little use, because of their being unsatisfactory from other points of view. Very high substantivity in a " naphthol " is not necessarily an advantage, except for package dyeing in machines. However, the affinity of " naphthols " of varying constitution for cellulose is of considerable interest.[53, 66]

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[64] *Melliand Textilber.* **20,** 63 (1939); see also Pokorny, *J. Soc. Dyers Colourists* **42,** 345 (1926). For a similar application of azoic dyes to terylene, see ICI, Hardwick and Waters, BP 629,452.

[55] See p. 669.

[65] *J. Soc. Dyers Colourists,* **50,** 37 (1934).

[53] See p. 669.

[66] Venkataraman, *Presidential Address, Chemistry Section, Indian Science Congress,* 1945, p. 18.

Quantitative estimates of substantivity are difficult to make, since the substantivity of a " naphthol " is even less of an accurately measurable and absolute property than that of a direct cotton dye.[67] No simple washing test can be employed for examining the reversibility of the adsorption. The variation in the phenolic function of the hydroxyl group from naphthol to naphthol results in differences in solubility in caustic soda and in the stability of the alkaline solutions. Substantivity is related to colloidal character in aqueous solution, and is affected by temperature, caustic soda concentration, and the presence of surface-active agents and protective colloids. If these factors are manipulated in order to prepare stable solutions for substantivity determinations, the figures are not strictly comparable. Difficulties in dissolving naphthols are often remediable by the use of alcohol, but the increased dispersion due to increasing percentages of alcohol progressively reduces the substantivity. Nevertheless, the influence of constitution on the substantivity of the " naphthols " is clearly recognizable.

Moryganov and Rostovtsev[68] have examined the relationships between the substantive properties of the anilide, *m*-nitroanilide and *p*-anisidide of BON acid (Naphtols AS, AS–BS and AS–RL) and the conditions of naphtholation, such as the amount of alkali, temperature and additions of alcohol, pyridine, formaldehyde and protective colloids. It was found that variations of alkali from 3–4 to 12–14 moles per mole of " naphthol " had very little effect on the substantive properties of the naphtholates. Within this range Naphtols AS and AS–BS were characterized by a small maximum in absorption, which was not observed with Naphtol AS–RL. Addition of alizarin oil increased as a rule the substantivity of the Naphtols in alkaline solution. Additions of alcohol, pyridine, gelatine and glue decreased the substantivity. Salt sharply increased the substantivity, while addition of formaldehyde decreased the substantivity of Naphtol AS and AS–RL, but increased it for AS–BS. The substantivity of the Naphtols decreased with rise in temperature. According to Nabar *et al.*[69] the adsorption of " naphthols " increases, reaches a maximum, and then decreases on adding increasing amounts of sodium hydroxide, chloride, sulfate and phosphate, and soap. The rate of adsorption was found to be greater at higher than at lower temperatures; the equilibrium adsorption increased with rise of temperature, and the amount of increase of adsorption for a particular range of temperature was greater at lower than at higher temperatures.

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[67] See Chapter XLI.

[68] *Trans. Inst. Chem. Technol. Ivanovo* (*USSR*) No. 2, 96 (1939); see also Giles, *J. Soc. Dyers Colourists* **60**, 280 (1944).

[69] *Proc. Indian Acad. Sci.* **10A**, 344 (1939).

Figures 1 and 2 represent the substantivities of the Naphtol AS range, determined under the stated conditions.[70] The curves illustrate clearly the very wide variations in substantivity.[71] With the less substantive Naphtols the absorption is only about 10–20%, while Naphtols AS–GR, AS–SG and AS–SR are almost completely absorbed.

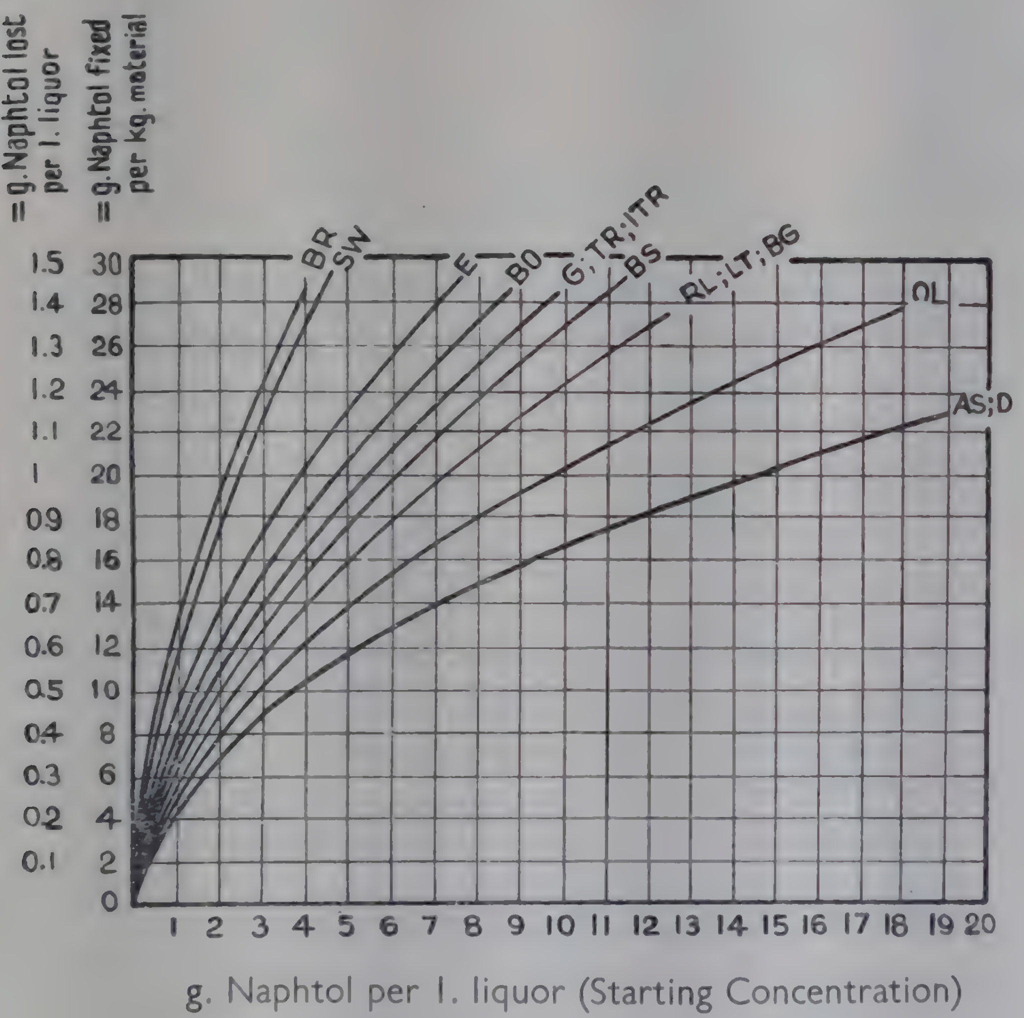

Fig. 1. Substantivity of the Naphtol AS range.

Length of liquor 1:20; material Lousiana 2/40's; temperature 30°. Naphtol AS-G with salt addition (30 g. calcined Glauber salt per liter).

Starting with an arylamide of an *o*-hydroxycarboxylic acid as the basic skeleton, compounds which are entirely benzenoid have poor substantivity and can only be applied to cotton with the aid of salt (cf. Cibanaphtol SB).

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[70] *IG Manual for Dyeing of Cotton*, 1936, p. 538.

[71] For the preparation and estimation of the substantivity of a large number of amides and anilides of hydroxynaphthoic acid, see Scheel, Dissertation, Univ. of Frankfurt, 1927.

Adequate technical substantivity, evidenced by the continued use of Naphtol AS, is obtained in the anilides of BON acid. Minor increases in substantivity can then be produced by the introduction of halogen atoms, methoxyl and nitro groups; C-alkyl groups have little or no effect.[72] Chlorine in the *p*-position is particularly effective; the *p*-chloroanilide (Naphtol AS–E) has the highest substantivity among the commercial anilides of BON acid. The influence of the position of the substituent is shown by the greater substantivity of the *p*-anisidide (Naphtol AS–RL) in comparison with the *o*-anisidide (Naphtol AS–OL). The substantivity of Naphtol AS–TR, which has a *p*-chlorine atom, is equalled by Naphtol

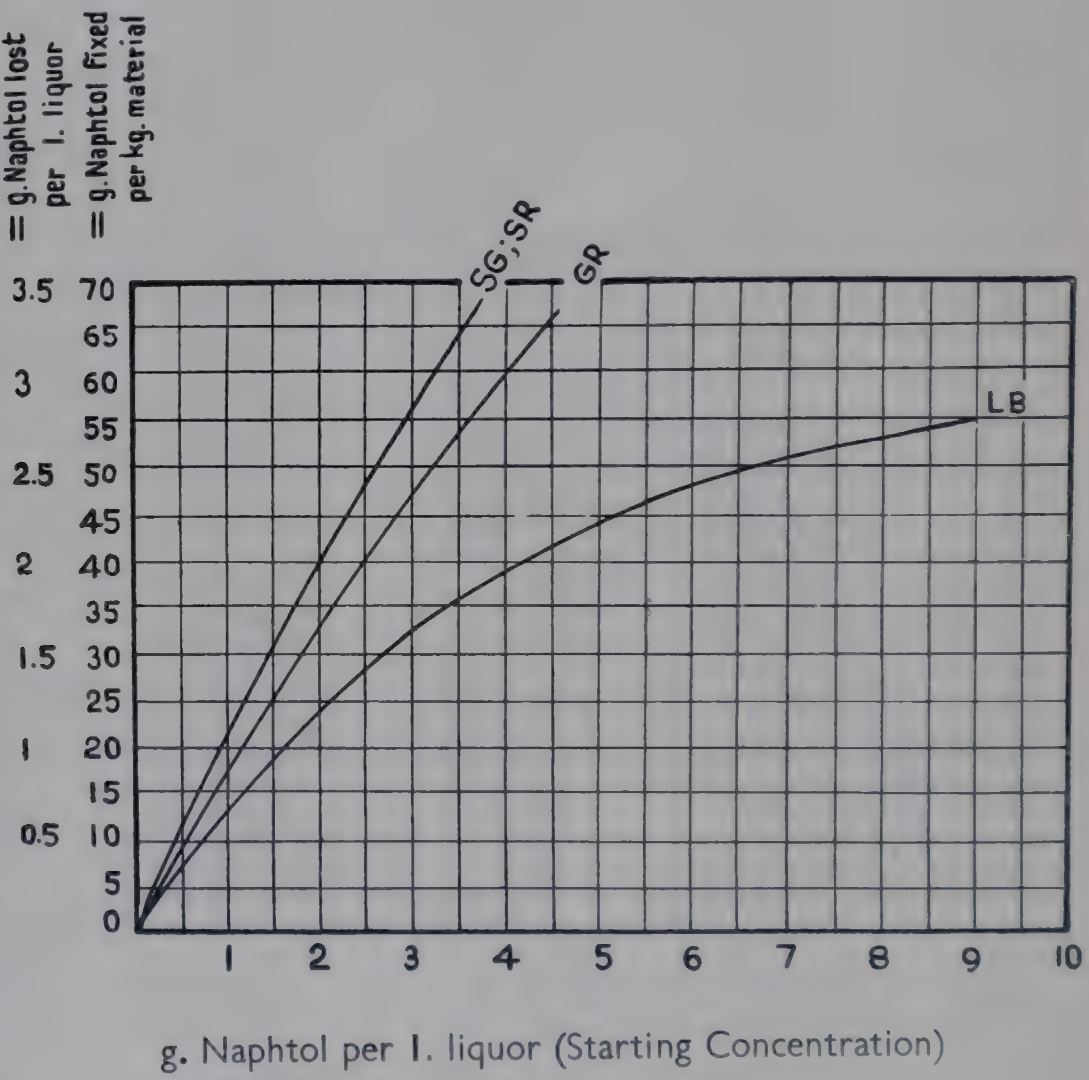

Fig. 2. Substantivity of the Naphtol AS range.

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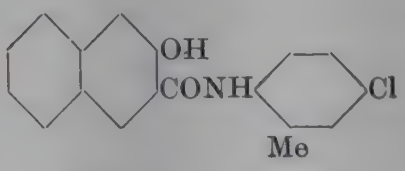
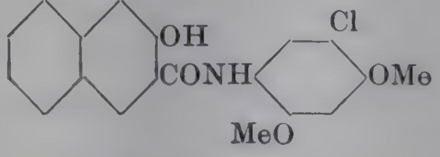
[72] See also Mangini and Andrisano, *Pubbl. ist. chim. ind. univ. Bologna*, No. 8, 3; No. 9, 3 (1943).

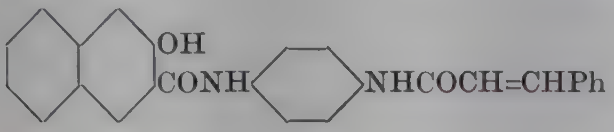
AS–ITR which has two methoxyl groups in conjunction with a chlorine atom *meta* to the amide group. The *p*-nitroanilide is more substantive than the *m*-isomer, although in view of other considerations the latter



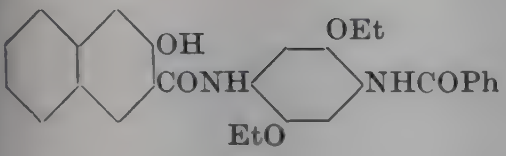
Naphtol AS–TR



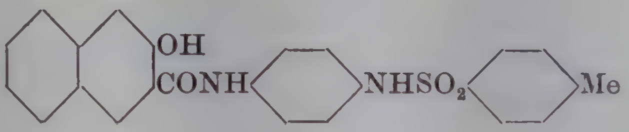
Naphtol AS–ITR



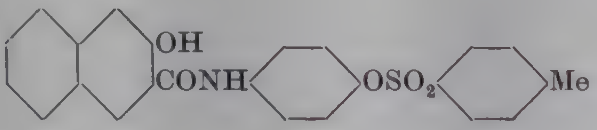
(I)



(II)



(III)



(IV)

(Naphtol AS–BS) is a widely used commercial product, and the *p*-nitroanilide is not marketed. The introduction of a second acylamido group increases substantivity; there is further increase by the presence of a double bond conjugated with the acyl group, as in *N*-cinnamoyl *N′*-hydroxynaphthoyl *p*-phenylenediamine (I). The additive effect of ethoxyl and benzamido groups is seen in the high substantivity of (II). The low substantivity of the "naphthol" (III) can be ascribed to the sulfonamide group, which is responsible for the ready solubility of the naphthol in alkali and the non-colloidal character of the solution. When the *p*-toluenesulfonyl group is present as an ester (IV), the "naphthol" has high substantivity.[27]

The replacement of aniline by benzidine results in a marked increase in substantivity. In the light of the influence of *o*- and *m*-substituents in benzidine and of groups separating the benzene rings mentioned in connection with the direct cotton colors, parallel effects in the Naphtol AS series have been investigated by the condensation of BON acid with *o*- and *m*-tolidine, *o*- and *m*-chlorobenzidine, diaminodiphenylmethane, diaminoazobenzene, and benzidine-sulfone.[73, 27] In general the orientations which render the azo dyes unsubstantive are unfavorable to substantivity in the "naphthols"; but substantivity is by no means destroyed in the hydroxynaphthoyl derivatives of the *m*-substituted benzidines or diaminodiphenylmethane, and none of the compounds of the series has lower substantivity than Naphtol AS. The derivatives of *m*-tolidine and *m*-dichlorobenzidine are in fact much more substantive than Naphtol AS.

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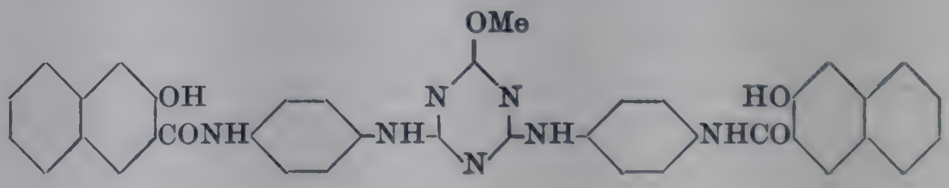
[27] See p. 655.

[73] Bhat and Patel, unpublished work.

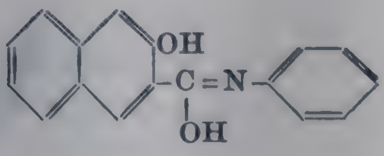
The transition from the anilide to the naphthylamides of BON acid represents a considerable increase in substantivity. The β-naphthalide (Naphtol AS–SW) is much more substantive than the α-isomer, the former having nearly the same substantivity as the bis-dianisidide (Naphtol AS–BR). The bis-hydroxynaphthoyl derivatives of some diaminonaphthalenes have been synthesized and found to have substantivities of the same order as Naphtol AS–SW.[73]

Replacement of the naphthalene nucleus in Naphtol AS by carbazole as in Naphtol AS–LB results in a great increase in substantivity; the anthracene derivative (Naphtol AS–GR) has still higher substantivity; and among the commercial Naphtols the maximum substantivity is possessed by Naphtol AS–SG and Naphtol AS–SR, two derivatives of 1,2-benzocarbazole. The increasing substantivity of "naphthols" derived from benzene, naphthalene, carbazole, anthracene and benzocarbazole would appear to be related to the resonance characteristics of these ring systems; it is also significant that with increasing complexity of the fused ring systems, there is a progressive increase in light absorption.[67]

Heterocyclic rings containing oxygen, nitrogen and sulfur are favorable to substantivity. The examples of Naphtol AS–L4G, AS–SG and AS–SR have been quoted; and there are numerous patents in which substantivity is sought to be increased by the introduction of hetero elements in the ring systems, especially in attempts to produce substantive β-ketonic acid arylamides for yellow shades. The condensate of BON acid and α-aminopyridine is more substantive than Naphtol AS–SW; the 2-aminothiazole



(V)



(VI)

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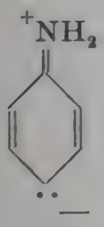
[73] See p. 677.

[67] See p. 674.

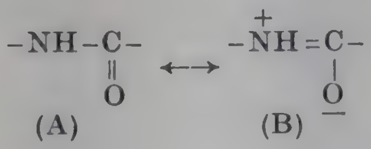
analog is intermediate between Naphtols AS and AS–SW.[27] "Naphthols" prepared by the condensation of cyanuric chloride with the aminoanilides of salicylic and BON acids (e.g., V) are highly substantive.[74]

The substantivity of Naphtol AS has been attributed[75] to enolization of the –CONH– group and conjugation as in (VI); but the constitutional factor fundamental to the substantivity of the "naphthols" is the hydroxyl adjacent to the –CONH– group, and this must play a part in the attachment to cellulose. The essentiality of the 2-hydroxy-3-carboxyamide group and the non-substantivity of the isomers are probably concerned with steric factors governing the attachment of the reactive centers in the "naphthol" to the cellulose chain.

The hypothesis of Schirm that enolization of the amide group extends the conjugation has been criticized[76] on the ground that, if the acylation of an amino group results in the extension of the conjugated chain, it should also have a bathochromic effect, which is contrary to the well-known fact that the color of a dye is lightened by acylation of an amino group. This criticism is not valid; while extension of a conjugated chain usually has a bathochromic effect, other considerations show that in this case there is an over-riding hypsochromic effect. The light absorption of aniline is associated with resonance structures such as (VII). Acylation of the amino group will destroy its auxochromic character; because of the amide resonance (VIII) or the tautomerism (IX), the unshared electron pair of the nitrogen atom will no longer be available for resonance structures such as (VII). However, unlike the anilinium ion which has a spectrum nearly identical with that of benzene, benzanilide absorbs at higher wave length than benzene. The absorption of benzanilide is defined by the sum of the absorption characteristics of the benzene ring conjugated with the carbonyl group (the Ph–C=O chromophore) and of the Ph–N=C chromophore; the contributions of these chromophores depend on the contributions of (A) and (B) to the amide resonance or the amide-enol tautomerism.

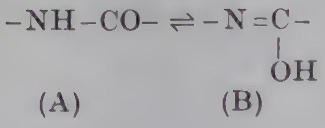


(VII)



$$\underset{(A)}{-NH-\underset{\overset{\|}{O}}{C}-} \longleftrightarrow \underset{(B)}{-\overset{+}{N}H=\underset{\overset{|}{\underset{-}{O}}}{C}-}$$

(VIII)



$$\underset{(A)}{-NH-CO-} \rightleftharpoons \underset{(B)}{-N=\underset{\overset{|}{OH}}{C}-}$$

(IX)

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[27] See p. 655.

[74] Shah and Talavdekar, unpublished work.

[75] Krzikalla and Eistert, *J. prakt. Chem.* (ii), **143**, 50 (1935); see also Schirm, *ibid.* **144**, 69 (1935).

[76] Rodd, Davidson and Stocks, *Annual Repts. Soc. Chem. Ind. London* **21**, 106 (1936).

Whatever the relative contributions may be, and whether benzanilide exists substantially in the enolic form or not, the introduction of the benzamido group has a bathochromic effect on benzene.

Rath and Burkhardt[77] have observed that BON acid and its *N*-methyl and *N*-ethyl anilides are considerably less substantive than Naphtol AS. *N*-Alkylanilides of BON acid are difficult to dissolve in aqueous alkali even in presence of dispersing agents. The sparing solubility of the *N*-alkyl derivatives of Naphtol AS in alkali may be related to the strength of the hydrogen bond between the 2-hydroxyl and the carbonyl group, owing to the hyperconjugation effect of the *N*-methyl group which makes

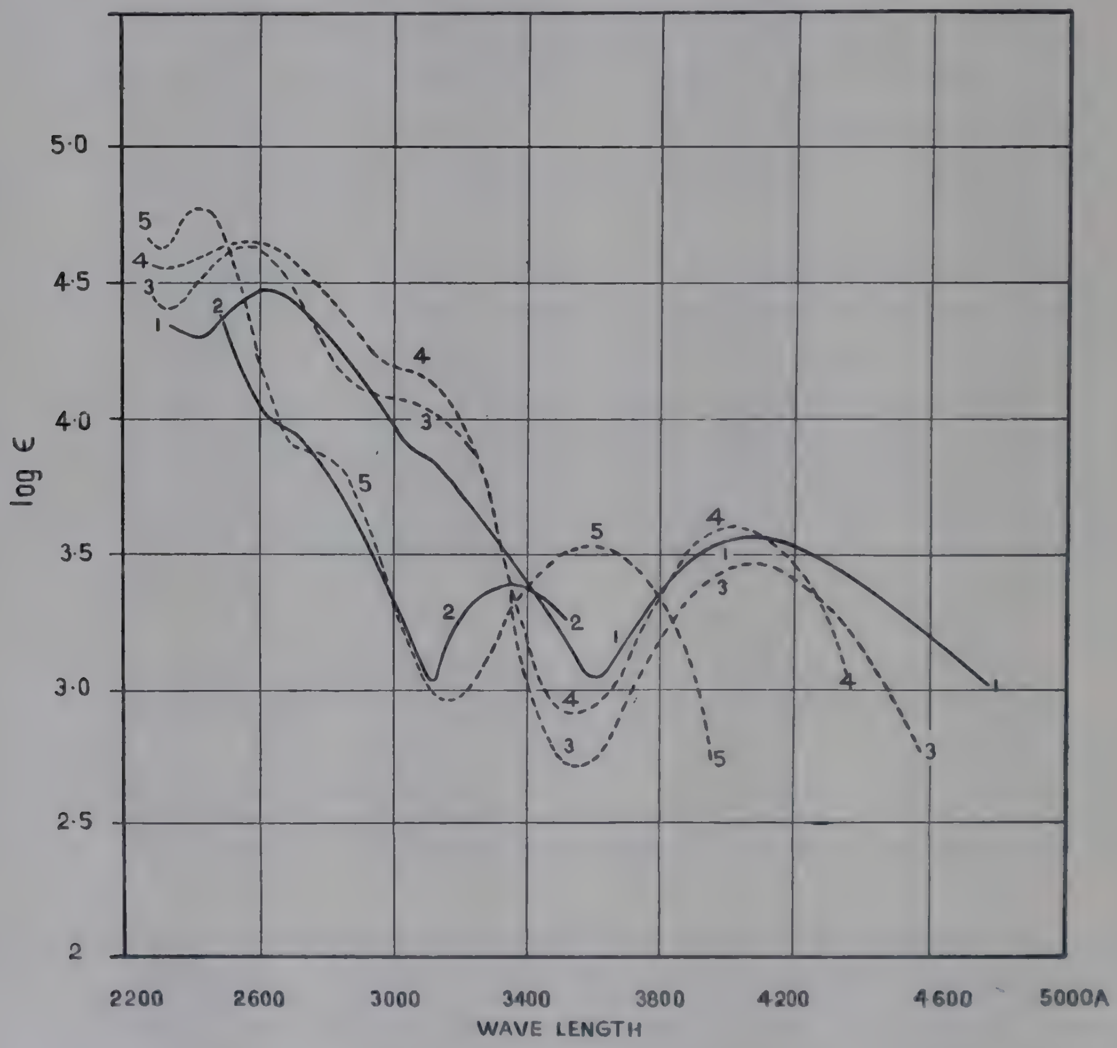

Fig. 3. Absorption spectra.

(1) Anilide of BON acid in alcohol;
(2) *N*-methylanilide of BON acid in alcohol;
(3) Anilide of BON acid in aqueous caustic soda;
(4) Anilide of BON acid in alcoholic caustic soda;
(5) *N*-methylanilide of BON acid in alcoholic caustic soda.

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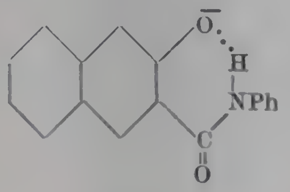
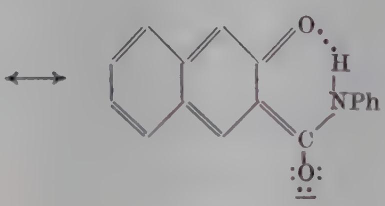
[77] Ber. **73B,** 701 (1940).

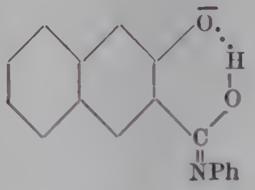
an unshared electron pair of the carbonyl oxygen more available for hydrogen bonding. Further, enolization of the amide group would augment the acid character of Naphtol AS, while in the *N*-alkylanilides the possibility of such enolization has been eliminated. Azoic shades from the *N*-alkylanilides are much weaker and much less fast to soaping than the corresponding shades from Naphtol AS.[78] The absorption spectra of Naphtol AS and its *N*-methyl derivative in neutral and alkaline solution are shown in Fig. 3. Naphtol AS exhibits two absorption maxima in neutral alcohol, aqueous caustic soda or alcoholic caustic soda. The absorption curves of the *N*-methyl derivative indicate a marked hypsochromic effect. Since there is a simultaneous decrease in affinity for cellulose, there is probably a common factor responsible for both the variations in the properties of Naphtol AS and its *N*-methyl derivative; this may be due to the enolisation possible only in the former. The substantivity of Naphtol AS and its analogs refers to the naphtholate ion, and not to the undissociated compounds. In view of the observation regarding azo dyes that, at least among the limited number of dyes examined, *o*-hydroxyazo dyes are more strongly absorbed than the *p*-isomers,[79] chelate structures such as (X) and (XI) may be involved in the orientation of the Naphtol AS ion at the water-cellulose interface; the chelate hydrogen bond is then replaced by hydrogen bonding between the anilide and cellulose molecules. In the isomers of Naphtol AS in which the hydroxyl and amide groups are not in adjacent positions, and in the *N*-alkylanilides, chelation in the naphtholate ion cannot be postulated. The substantivity of the leuco compound of 1-benzamidoanthraquinone in contrast to the 2-isomer is open to a similar interpretation.



(XA)



(XB)



(XI)

FASTNESS PROPERTIES OF AZOIC SHADES

Fastness to rubbing. The nature of the dyeing process indicates that the main problem in azoic dyeing is the superficially precipitated pigment, the effect of which is lack of fastness to rubbing (or crocking). Careful control of the conditions of naphtholation, development and after-treatment is necessary for producing shades of good fastness to rubbing.[53]

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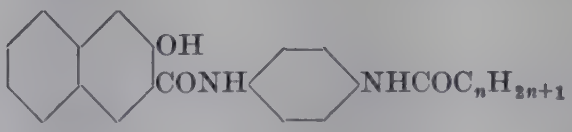
[78] Modak and Rao, unpublished work.

[79] Ruggli and Jensen, *Helv. Chim. Acta* **18,** 624 (1935).

[53] See p. 669.

Two factors play a dominant role in determining the rubbing fastness of an azoic dyeing. One is the substantivity of the "naphthol," since it is the "naphthol" not substantively adsorbed but mechanically retained by the yarn, which is responsible for the rubbing-off effect. The other is the efficiency of the removal of the azoic pigment by the soaping aftertreatment. Aqueous solutions of soaps and synthetic detergents have a solvent action on organic compounds sparingly soluble in water; the grease, oil or other organic substance forms a liquid solution in the aggregates or micelles formed by the paraffin chain ions of the detergent at a critical concentration range.[80] The solubilization of azoic dyes by pure soaps and detergents of different types has been studied by McBain,[81] but the significance of their data in the aftertreatment of azoic dyeings has not been discussed. The solvent action of aqueous soaps and detergents has a bearing on the aftertreatment of azoic dyeings. The aftertreatment with soap or synthetic detergent solution is usually regarded as a process of emulsification of the superficially precipitated azoic pigment formed from that part of the "naphthol" not substantively adsorbed and not removed by hydroextraction; solubilization must be assumed to be at least partially responsible for the action.[82] From this point of view the introduction of a long paraffin chain in the "naphthol" or diazonium component may be expected to yield azoic shades with increased rubbing fastness. "Naphthols" of this type (e.g., I; $n = 5$–17) have been synthesized.[77, 82] Being built partly on a soap basis and of comparatively high molecular weight, colloidal character in aqueous alkali is a well-marked property of these "naphthols," which exhibit good affinity for cellulose. The azoic dyeings from them have excellent fastness to rubbing, but the practical application of the "naphthols" is limited by the difficulty in dissolving them.



(I)

Fastness to alkali. This is an important consideration for azoic and vat dyes on cotton, since dyed yarn may be woven with undyed yarn and the fabric then scoured in a kier with an alkaline liquor, usually soda ash and soap (or other detergents) at about 60°. It is necessary that the dyes should withstand more stringent treatment, providing a margin of safety. The action of boiling caustic soda solution on insoluble azo colors on the fiber has been the subject of extensive work by Rowe.[83] Dyeings on bleached cotton yarn were plaited with an equal weight of the undyed material and refluxed with 0.36% caustic soda solution (material liquor ratio of 1:10) for 6 hours; the appearance of the samples was then examined, and the dyeings were arranged in five grades. None of the azoic colors Rowe examined was found to merit the fifth grade of " excellent " which represented no alteration in depth and tone. The products of degradation of azoic colors in the kier by the reducing action of cellulose and the impurities in the fiber in presence of boiling alkali were also investigated. Three conclusions were drawn: (1) looseness to kier boiling is the result of aggregation and migration of the dye particles, which may be accompanied by hydrolytic and reductive decomposition; (2) the presence of a nitro group in the dye invariably has an unfavorable influence on the fastness to kier boiling; and (3) resistance to kier boiling is a specific property of an azoic dye, which cannot be resolved into the property of either component. In the search for combinations to resist kier boiling, Bean and Rowe[61] considered that the ease of aggregation and subsequent migration of the coloring matter in the fiber can be taken as a reliable guide, for combinations which aggregate and migrate readily are also bound to bleed and mark off during kier boiling. Azoic dyes are generally resistant to hypochlorites, but vary widely in their resistance to kier boiling with caustic soda; they also mark off with certain types of softeners used in finishing, especially during hot calendering.[84]

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[80] Hartley in Wetting and Detergency, p. 153, Harvey, London, 1937; McBain, Alexander's Colloid Chemistry, Vol. V, Reinhold, New York, 1944.

[81] Green and McBain, *J. Phys. Colloid Chem.* **51**, 286 (1947); and earlier papers.

[82] Bhat, Ramachandran and Venkataraman, *J. Soc. Dyers Colourists* **58**, 203 (1942).

[77] See p. 680.

Rowe's observations have been extended by experiments in a kier under conditions approximating closely to those prevailing in technical practice, as well as drastic conditions of boiling under pressure in a kier with a solution containing soda ash and caustic soda.[43] From a study of numerous azoic combinations, both from commercial Naphtols and from newly synthesized analogs, certain correlations were observable between fastness to kier boiling and the presence of specific groups in the azoic components. No relation can be traced between the substantivity of a Naphtol and the fastness to kier boiling of a dye derived from it. The effect of kier boiling on the great majority of azoic colors on the fiber is to dull the shades. Maintaining the diazonium component constant, it was found that alkyl, halogen, alkoxyl and benzamido groups in the arylamine part of a " naphthol " have usually the effect of augmenting the kier-boiling fastness. Thus Naphtol AS–D is slightly superior to Naphtol AS, the former being the *o*-toluidide. Dyeings from Naphtols AS–OL, AS–RL, AS–TR and AS–ITR, which contain methoxyl and chlorine substituents, are faster than the corresponding shades from AS–D. The α-naphthalide (Naphtol AS–BO) is superior to the β-isomer (Naphtol AS–SW). The favorable influence of a benzamido group is shown by the excellent fastness to kier boiling of dyeings from "naphthols" containing additional benzamido groups. The benzamido group is also useful when present in the diazonium component, since Fast Blue Salt BB combinations are generally fast to kier boiling. The position of the benzamido group is also important. The dyeings from Fast Blue Salt BB are superior to those from Fast Red Salt RBE, the benzamido group being *para* and *meta* respectively to the azo group in the dyes. Symmetrically constituted naphthols like Naphtol AS–BR give dyeings with high fastness to kier boiling. "Naphthols" containing a diphenylamine skeleton are also fast. "Naphthols" of the acetoacet-arylamide type are characterised as a class by high resistance to alkali boil, as shown by the very good fastness of dyeings from Naphtols AS–G, AS–LG and AS–L3G. A ketonic group in a "naphthol" of the normal type has a favorable influence; the dyeings from the hydroxynaphthoyl derivatives of *p*-aminoacetophenone and *p*-aminobenzophenone have high fastness to kier boiling. Neither the experimental evidence for a large number of azoic combinations nor theoretical considerations support the suggestion[85] that the inferior fastness of AS–SR combinations, in comparison with AS–SG combinations, is due to the high potential energy of the dyestuff in the solid phase as a result of the methyl group in AS–SR preventing the close packing of the arylamine residue and the close approach of the associative amide groups.

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[83] Rowe, *J. Soc. Dyers Colourists* **47,** 29 (1931); Rowe and Ueno, *ibid.* 35; Rowe and Jowett, *ibid.* 163; Rowe and Giles, *ibid.* **51,** 278 (1935).

[61] See p. 672.

[84] Blackshaw, *ibid.* **52,** 9 (1936).

[43] See p. 659.

Fastness to light. In carrying out light fastness tests it is important to compare dyeings of the same depth of shade since the fastness of an azoic combination deteriorates with lighter dyeings. The light fastness of an azoic dye is dependent on both the components, and one reason for the technical use of only a relatively small fraction of the more than thousand azoic combinations that are available is that the fastness to light varies from 1–2 for some of the shades from Naphtol AS–G to 7–8 for a few of the shades from Naphtol AS–SG, AS–SR and AS–L4G.[85a] Naphtol AS with Fast Scarlet GG, Fast Red GL or Variamine Blue B gives dyeings very fast to light, while the shade from the same Naphtol and Fast Red RBE is poor in light fastness. Dyeings poor in light fastness are obtained with Naphtol AS–G and Fast Bordeaux GP, whilst Naphtols AS–BO,

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[85] Preston, Turner and Wall, *Annual Repts. Soc. Chem. Ind. London* **23**, 221 (1938). An interesting example of a slight modification in structure resulting in considerably increased fastness is the claim that the replacement of the methyl by the ethyl group in Naphtol AS-TR leads to decreased "bleeding and fading" of the azoic shades (Lecher and Adams, USP 2,468,600).

[85a] Talavdekar finds that the light fastness of the azoic shades from Naphtol AS–L4G and Fast Yellow GC, Scarlet GG, Red KB and B is only 4-5.

AS–SW and AS–RL give very fast dyeings with the same diazonium salt. When a Fast Base and a Naphtol, each of which has a low figure for the average light fastness, are combined, the resultant azoic shade has a considerably lower fastness than the average for either component. On the other hand, there are Fast Bases and Naphtols which give azoic dyes of higher light fastness than the average figure for either component; an example is the azoic shade Naphtol AS–ITR/Fast Red ITR, which has a fastness of 7, while the average figure for the Naphtol is 6 and for the Base 5. Such examples of the specificity of the light fastness of azoic dyes can be multiplied, but at the same time certain general trends can be observed.

Table V gives the average light and chlorine fastness of a series of Naphtols and Fast Salts in combination with each other. The figure for each Naphtol is the average of the fastness figures for the azoic dyes produced by coupling the Naphtol with 33 Fast Salts; and the figure for each Fast Salt is the average of the fastness figures for the azoic dyes produced by coupling 16–24 Naphtols with the Fast Salt. For the newer Naphtols AS–BT, AS–S, AS–LG, AS–L3G and AS–L4G the figures are less representative, and refer only to the combinations which are specially recommended for use. This is also true of the newer Fast Bases or Salts: Scarlet VD and LG, Red F3G and GTR, Golden Orange GR, Orange GGD and LG, Bordeaux BD, and Variamine Blue FG. All the figures are taken from IG publications.

α-Aminoanthraquinone stands out among all the Fast Bases for the uniformly high light fastness of the azoic shades derived from it. The Fast Bases (Orange GGD and RD; Golden Orange GR; Scarlet VD) containing a trifluoromethyl group yield shades with excellent light fastness. Examples of the high light fastness of such azoic combinations in full shades are: AS–OL and Orange GGD (6–7); AS–L3G and Orange RD (6–7); AS–L4G and Orange RD (7–8); AS–LC and Orange GR (7); AS–RL and Orange GR (6–7); AS and Scarlet VD (6–7); AS–E and Scarlet VD (6). The Fast Bases containing an alkyl or aralkyl sulfone group (Orange LG, Scarlet LG and Red GTR) also yield shades with very good light fastness. Chloroanilines give fast dyeings with most of the Naphtols. Fast Scarlet 2G (2,5-dichloroaniline) gives faster dyeings than the monochloroanilines. Although faster dyeings are obtained from Fast Orange GR (*o*-nitroaniline) than from Fast Yellow GC (*o*-chloroaniline), Fast Orange GC (*m*-chloroaniline) yields faster dyeings than Fast Orange R (*m*-nitroaniline). Chlorine atoms and nitro groups are more favorable to light fastness if present in the diazonium component than in the Naphtol component. The position of these groups with respect to the amino group in the base is important. They impart better fastness properties when present in the *o*- or *p*-positions to the amino group than in the *m*-, the *o*-position being more effective than the *p*-. Nitrotoluidines and nitroanisidines, in which the nitro and amino groups are *o*- or *p*- to each other, yield shades of good light fastness. Benzidine and its derivatives and aminoazo compounds as Fast Bases lead to low light fastness.

Considering the Naphtols, Naphtol AS–L4G shades possess excellent fastness to light, although the figure of 6–7 in Table V is somewhat illusory because of the limited number of shades taken into account.[85a] Apart from the ethoxyl group and the benzothiazole nucleus, the favorable factor for light fastness in the AS–L4G shades is the formation of a monoazo dye. A second azo group in an azoic dye is usually unfavorable to light fastness, but in the dyes derived from AS-L3G, this is compensated by the influence of the chlorine atoms and the methyl and methoxyl groups. The azoic dyes from the carbazole and benzocarbazole derivatives (AS–LB, AS–SG, AS–SR) possess very high light fastness. Among the arylamides of BON acid, the 5-chloro-2,4-dimethoxyanilide (Naphtol AS–ITR), apparently by virtue of this specific substitution, yields shades of very good light fastness (average figure 6). The isomeric compound (4-chloro-2,5-dimethoxyanilide; AS–LC) is slightly inferior to AS–ITR. The favorable influence of a methoxyl in the *o*- or *p*-position to the amide linkage is also shown by the high light fastness figures for the *o*- and *p*-anisidide (AS–OL; AS–RL), the 2,5-dimethoxyanilide (AS–BG), and the 4-methoxy-2-methylanilide (AS–LT). The dibenzofuran nucleus appears to be a useful factor in either the acid or amine half of a "naphthol"; both Naphtol AS–BT and AS–S have a light fastness figure of 5–6. The anilide, chlorotoluidide, α- and β-naphthalide of BON acid yield shades of good light fastness (5). The lower light fastness of the shades from the *p*-chloroanilide (AS–E), in comparison with the parent anilide (AS) and the 2-methyl-*p*-chloroanilide (AS–TR), is of interest. The lowest average light fastness (3–4) among the Naphtols is represented by the shades from the diacetoacet-*o*-tolidide (AS–G) and the anthracene derivative (AS–GR).

Fastness to chlorine. In Table V the Naphtols and Fast Bases or Salts have been arranged in groups of decreasing fastness to light of the azoic dyes derived from them, but they have not been arranged in this manner with reference to their fastness to chlorine. Considering the Naphtols, nearly all the arylides of BON acid in combination with a wide range of diazonium salts give azoic shades with an average chlorine fastness of 4; the 5-methoxy-*o*-toluidide (Naphtol AS–LT) is outstanding in its fastness. An exception among the arylides of BON acid is the *bis*-dianisidide (Naphtol AS–BR), the azoic dyes from which have average chlorine fastness of only 2–3. The two benzocarbazole derivatives (Naphtol AS–SG and SR),

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[85a] See p. 684.

TABLE V

FASTNESS OF AZOIC DYES TO LIGHT AND CHLORINE

Naphtol	*Average light fastness* (1–8 scale)	*Average chlorine fastness* (1–5 scale)	*Fast Base or Salt*	*Average light fastness* (1–8 scale)	*Average chlorine fastness* (1–5 scale)
AS–L4G	6–7	4	Red AL	6–7	4
AS–LT	6	4–5	Orange GR	6	4
AS–ITR	6	4	Scarlet GGS	6	4
AS–LB	6	3–4	Scarlet VD	6	4
AS–SG	6	4	Scarlet LG	6	4
AS–SR	6	4	Red RL	6	3–4
AS–OL	5–6	4	Red B	6	3–4
AS–RL	5–6	3–4	Red F3G	6	4
AS–BG	5–6	3–4	Orange RD	5–6	4
AS–LC	5–6	4	Orange GGD	5–6	4
AS–S	5–6	3–4	Golden Orange GR	5–6	3–4
AS–BT	5–6	3	Orange LG	5–6	4–5
AS–L3G	5–6	4	Red GG	5–6	3
AS	5	4	Red 3GL	5–6	4
AS–D	5	4	Red GL	5–6	4
AS–TR	5	4	Red GTR	5–6	4–5
AS–BO	5	4	Variamine Blue RT	5–6	3
AS–SW	5	4	Black LB	5–6	4
AS–LG	5	3–4	Yellow G, GC	5	4
AS–BS	4	4	Orange G, GC	5	4
AS–E	4	4	Orange R	5	4
AS–BR	4	2–3	Scarlet TR	5	4
AS–GR	3–4	3	Scarlet RC	5	4–5
AS–G	3–4	4	Scarlet G	5	4
			Red KB	5	4–5
			Red TR	5	4
			Red RC	5	4
			Red ITR	5	4
			Red FG	5	4
			Red FR	5	4
			Bordeaux GP	5	4
			Bordeaux BD	5	3–4
			Corinth LB	5	4
			Variamine Blue B	5	2–3
			Blue RR	5	3–4
			Blue BB	5	3–4
			Black K	5	4
			Corinth V	4–5	4
			Garnet GBC	4–5	4
			Violet B	4–5	3–4
			Variamine Blue FG	4–5	2
			Red RBE	4	4–5
			Garnet GC	4	4
			Blue B	3–4	3–4
			Black G	3–4	3

like the general run of the BON acid derivatives, have good fastness (4), but the carbazole derivative (Naphtol AS–LB) is slightly inferior (3–4). The yellow azoic shades from Naphtols AS–G, AS-L3G and AS–L4G have a figure of 4, while Naphtol AS–LG shades are slightly inferior. The dibenzofuran derivatives (Naphtol AS–BT and Naphtol AS–S) are represented by the figures 3 and 3–4. The anthracene derivative (Naphtol AS–GR) yields azoic dyes which have relatively low fastness both to light and chlorine.

The generally high average of the fastness of azoic dyes to chlorine is reflected also in the figures calculated from the point of view of the Fast Bases or Salts. One interesting feature is that for several Fast Bases there is a substantial difference in the fastness to light and to chlorine of the azoic shades. Fast Bases Red KB and RBE for instance yield azoic shades with an average chlorine fastness of 4–5, but with a light fastness of only 5 and 4. The aminodiphenylamines (Variamine Blues) give azoic shades of inferior chlorine fastness (2–3).

AZOIC COLORS IN PRINTING

Azoic dyes constitute in some ways the most important group of coloring matters available to the calico printer. They can be applied in printing by a variety of methods. Brightness is a quality specially prized in printing colors, and it is a characteristic of azoic dyes in which they are second only to the basic colors, while in their fastness properties the azoics are greatly superior to the basics. Some of the other advantages of the azoics in printing are that their insolubility in alkali renders them suitable for printing side by side with vat colors, and they are adaptable to direct, resist and discharge styles. Among the azoic colors derived from β-naphthol, Para Red has survived, being comparable in its brightness to Turkey Red, but much cheaper to produce and more suitable for bulk production under modern conditions; but in printing as in dyeing, the azoic dyes now employed mostly comprise the Naphtol AS type in conjunction with a wide range of diazonium components.

An azoic print may be produced by the application of the " naphthol " and diazonium components (a) separately as in dyeing processes or (b) simultaneously, in the form of special printing compositions. In the first or two-stage method again, there are several variations which are practised in accordance with the " style " desired and other considerations. (1) The pattern may be printed in an alkaline solution of the " naphthol " (suitably thickened by means of gum tragacanth, etc.), dried and developed by passage through the diazonium salt solution. (2) The fabric is " prepared " in the " naphthol," i.e., impregnated with the " naphthol " solution, dried, and the thickened diazonium solution printed. In both these methods it is obvious that by using different "naphthols" and diazonium salts, multicolored prints can be readily obtained. Printing pastes containing diazonium salts and carbohydrate thickeners tend to become less viscous on keeping; the addition of various substances to prevent thinning of the pastes has been suggested, and one example is *N*-vinylacetamide.[86] (3) The fabric is naphtholated, printed with a resist (e.g., formaldehyde-sulfoxylate) which will destroy the diazonium salt, and then developed with the diazonium salt. (4) The fabric is dyed an azoic shade, and the pattern produced as a discharge by printing with a reducing agent (usually a thickened mixture of formaldehyde-sulfoxylate and alkali), and then steaming. The reducing agent destroys the azoic dye and produces a white effect; and a colored discharge can be produced by adding to the reduction mixture a dyestuff (e.g., a vat dye) which is not destroyed by the reducing agent. Printing being a complicated art, other variations in these procedures are possible and are practised.

Printing compositions. Although the two-stage route to azoic prints continues to be followed, the scope of the azoic dyes in printing has been greatly extended by the introduction of ready-made printing compositions, which contain both the "naphthol" and diazo components under conditions inhibiting the coupling reaction. The printer has only to make up the mixture with a thickener, apply it to the fabric, and develop the print by suitable treatment for the azoic components to couple. Diazonium salts may be stabilized in two distinct forms: (1) as sulfates, double salts, etc., which are capable of coupling as soon as they are dissolved in water, and (2) as anti-diazotates, etc., which are stable under alkaline conditions and which have to be submitted to acid or other treatment to convert them into the labile form capable of coupling.[87] The first type of stabilized diazonium salt is valuable for dyeing and for printing by the two-stage method. The second type in admixture with alkali naphtholates is used in printing compositions. A process for printing with an alkaline mixture of β-naphthol and a nitrosamine was patented in 1894 by BASF, and after the advent of the Naphtol AS series the process, with subsequent modifications, acquired great importance. The Rapid Fast colors were introduced in 1914-15 by GrE, followed by the Rapidogens in 1930 and the Rapidazols in 1932.

Rapid Fast colors. The stabilization[87] of the diazo compound in the Rapid Fasts is in the form of the nitrosamine or alkali anti-diazotate, and the current range of the Rapid Fast colors, together with their composition, is listed in Table VI.[4] The identity of the coupling components in such printing mixtures can be determined by acidifying them, filtering off the precipitated " naphthol " which is then identified, and coupling the diazonium salt in the filtrate with alkaline β-naphthol.[88] The azoic dye is then compared with the azoic dyes from β-naphthol and known diazonium salts which have been prepared and characterized for this purpose. The " naphthols " used for admixture with stabilized diazo compounds in the

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[86] Adams and American Cyanamid, USP 2,497,890.

[87] See Chapter IV.

[4] See p. 651.

TABLE VI

COMPOSITION OF RAPID FAST COLORS

Rapid fast	*Naphtol*	*Base*
Yellow GGH	AS–G	Red RC
Yellow GH	AS–G	Scarlet GG
Yellow I3GH	(I)	Red TR
Golden Yellow IGH	(II)	Red RC
Orange GH	AS–D	Orange GC
Orange IGH	AS	Orange RD
Orange IRH	AS–OL	Orange RD
Orange RG	AS	Orange GR
Orange RH	AS–PH	Scarlet GG
Golden Orange IGG	AS–D	Golden Orange GR
Scarlet ILH	AS–OL	Scarlet GG
Scarlet RH	AS–PH	Red KB
Red B	AS	Red B
Red BB	AS–BS	Red B
Red FGH	AS–D	Red KB
Red GG	AS	Red GG
Red GL	AS	Red GL
Red GZH	AS	Scarlet GG
Red I3GL	AS	Red 3GL
Red ILB	AS–RL	Red RL[88a]
Red IRH	AS–LT	Red TR
Red RH	AS–OL	Red RC
Bordeaux IB	AS–BOX (undissolved AS–BO)	Red B
Bordeaux RH	AS–BS	Red RC
Blue B	AS	Blue B
Brown B	AS	Blue B+Red GG
Brown GGH	AS–LB	Scarlet GG
Brown IBH	AS–LB	Red RC
Brown IRH	AS–BG	Scarlet GG
Olive Brown IGH	AS–LB	Orange GC

Rapid Fast and Rapidogen colors mainly belong to the commercial range of Naphtols; but there are a few exceptions. The acetoacetarylides (I) and (II) in Tables VI and VII give fast yellow prints, but they do not possess adequate substantivity for use in dyeing as " naphthols " for yellow shades. The *o*-phenetidide of BON acid (Naphtol AS-PH), β-tetralolcarboxy-β-naphthylamide (III), 1-amino-4-benzeneazo-7-naphthol (IV) and the *o*-ethylanilide of 3-hydroxydibenzothiophen-2-carboxylic acid (V) are

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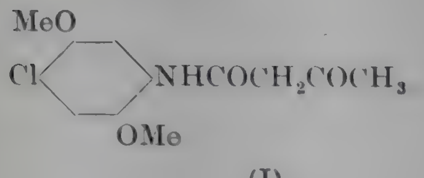
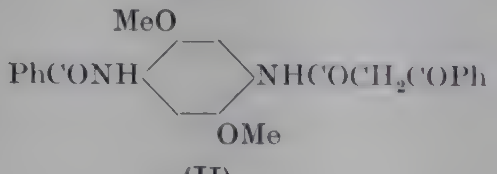
[88] Rowe *et al. J. Soc. Dyers Colourists* **37,** 204 (1921).

[88a] *FIAT* **1313,** II mentions Naphtol AS-LT and Red TR Base.


(I)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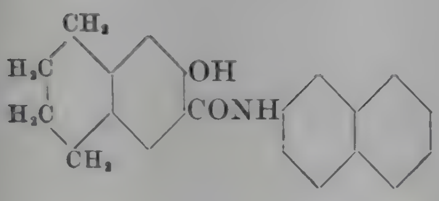
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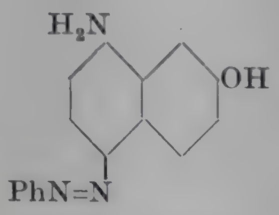
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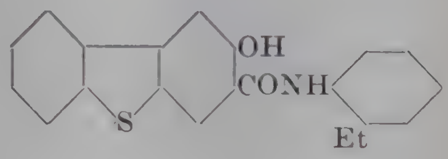
(V)

other "naphthols" which have so far been used only in printing compositions. The Rapid Fast range is limited because the nitrosamine method of stabilization is not applicable to all amines.

Marketed originally in paste form, the Rapid Fasts were later made available in powder form. In either form they have reasonable stability, but careful storage is necessary to avoid decomposition, as well as premature coupling; absorption of carbon dioxide for instance, if allowed to proceed far enough, will neutralize the excess alkali and effect coupling. The mixtures are not indefinitely stable; spontaneous isomerization of the stabilized diazo compound to the *syn*-diazotate, which then couples with the "naphthol," gradually takes place. For printing, the Rapid Fasts are thickened with starch-tragacanth; caustic soda is added to the powder brands. It is an advantage to add neutral chromate solution to avoid reduction of the diazo compound during ageing. The prints may be developed by neutral steaming for a few minutes, followed by passage through an acetic acid-Glauber salt bath, or by acid steaming in an ager to which vapors of acetic or formic acid (or a mixture of the two) are admitted. The second procedure gives brighter and fuller prints.

Rapidogen colors. The Rapidogens, which are tending to replace the Rapid Fasts, are mixtures of Naphtols (or the sodium naphtholates) with diazoamino compounds.[87] After standardizing by the addition of sodium sulfate, sodium benzenesulfonate, modified starch, etc., they are marketed as powders, which have much greater stability than the Rapid Fasts and other advantages. For printing, the Rapidogens are pasted with caustic soda solution, starch-tragacanth thickening and a sulfonated oil; and they are developed by acid steaming. Unlike the Rapid Fast colors which can be developed by alternative methods (e.g., even by merely hanging the printed fabric and allowing it to absorb atmospheric carbon dioxide), the treatment with steam containing acetic or formic acid is essential for the Rapidogens, because of the high stability of the diazoamino compound. The acid treatment is best carried out in a special acid ager or steamer consisting of a chest constructed of material which can withstand the corrosive action of the hot acid vapors; passage of the printed goods through the acid steamer effects rapid and continuous development. If an acid steamer is not available, two other procedures may be used: a wet developing process in which the printed material passes through a bath containing about 1% acetic acid, 0.5% formic acid and 5% Glauber salt at 95–100°; or a drying cylinder process in which the printed fabric is padded on the face with a similar and somewhat stronger solution at room temperature, and dried immediately at a moderate temperature on the usual cylinder drying machine. Rapidogen Developer N (diethylaminoethanol) and NN (diethylaminoethanol + calcium lactate) have been introduced by IG as aids in printing with the Rapidogen colors. Using Developer N, it is claimed that Rapidogens can be printed in juxtaposition to vat dyes. By incorporating Developer NN in the Rapidogen printing paste, acid steaming can be replaced by neutral steaming; thiodiglycol, a weak acid and a volatile substance of slightly alkaline reaction can be used for the same purpose.[89]

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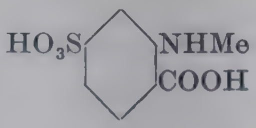
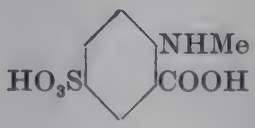
[87] See p. 689.

The Rapidogens cover a complete range of shades, including blue, corinth, violet and green. The Naphtol and diazo components, as well as the amino acids used for stabilizing the diazonium salts as diazoamino compounds, are stated in Table VII. The amino acids used are sarcosine (VI), *N*-methyltaurine (VII), 4-sulfoanthranilic acid (VIII), and its *N*-methyl derivative (IX), and the 5-sulfo-*N*-alkyl-anthranilic acids (X and XI).

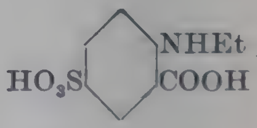
(IX)



(X)



(XI)



Rapidazols. Rapidazols are mixtures of Naphtols and aryldiazosulfonates, ArN_2SO_3Na.[87] For printing, they are pasted with caustic soda solution, neutral chromate solution and starch-tragacanth thickening; and the prints are developed by neutral steaming for a few minutes. Unlike the Rapidogens, the Rapidazols do not require acid steaming for development, but an oxidizing agent such as an alkali chromate is necessary for the ready liberation of the diazonium radical, which then reacts instantaneously with the Naphtol.

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[89] Lantz and St. Denis, FP 859,710.

[87] See p. 689.

TABLE VII
COMPOSITION OF RAPIDOGEN COLORS

Rapidogen	*Naphtol*	*Fast Base*	*Amino acid*
Yellow G	AS–G	Red KB	(VIII)
Yellow GS	AS–G	Red KB	(VI)
Yellow GG	AS–G	Red RC	(VI)
Yellow I4G	(I)	Red TR	(VII)
Yellow PT	AS–G	*p*-Tolylazoaminotoluene	
Yellow I3G Golden Yellow IGL	AS–L4G[90]	Red KB	(VI)
Golden Yellow IFG	(II)	Red RC	(VI)
Golden Yellow R	AS–G+AS–PH	Red KB	(VI)
Orange G	AS–D	Orange GC	(VIII)
Orange IGN	AS–OL	Orange GGD	(XI)
Orange IRR	AS–OL	Orange RD	(XI)
Orange R	AS–PH	Scarlet GG	(XI)
Golden Orange I2G	AS–D	Golden Orange GR	
Scarlet IL	AS–OL	Scarlet GG	(XI)
Scarlet R	AS–PH	Red KB	(VIII)
Scarlet RS	AS–PH	Red KB	(VI)
Red GS	AS–D	Red KB	(VI)
Red G	AS–D	Red KB	(VIII)
Red IGG	AS–LC	*o*-Toluidine-4-sulfondimethylamide	(X)
Red–ITR	AS–ITR	Red ITR	(XI)
Red R	AS–OL	Red RC	(VI)
Bordeaux IB	AS–BO	Red B	(X)
Bordeaux RN	AS–D	Red RL	(XI)
Corinth IB	AS–LT	Corinth LB	(IX)
Violet B	AS	Violet B	(VI)
Red Violet RR	AS–BO	6-Nitro-4-methoxy-*m*-toluidine	(XI)
Blue B, BN	AS	Blue BB	(VI)+50% (VII)
Navy Blue IB	AS	Variamine Blue B	(VI)
Navy Blue D	AS–D	Mixture of Blue Salts	(VI)
Blue R	AS	Blue RR	(VII)
Navy Blue B	AS	Blue B	(VII)
Navy Blue R	AS–BO	Blue RR	(VII)
		Blue BB	50% (VI)+50% (VII)
Green B	AS–GR	Blue BB	(VI)+(VII)
Brown GN	AS+AS–G	Azo Red Salt KBS+Azo Blue Salt RR	
Brown IB	AS–LB	Red RC	(VI)
Brown IBR	AS–LB	*p*-Toluidine	(VI)
Brown IR	AS–BG	Scarlet GG	(XI)
Brown IRRN	AS–LB	Red RL	(XI)
Olive Brown IG	AS–LB	Orange GC	(VIII)
Black Brown ITR	AS–BT	Red ITR	(XI)
Black Brown T	AS–BT	Red RC	(VI)
Black Brown IT	AS–BT+AS–ITR	Azo Red Salt RC	
Black IT	AS–SR+(III)	Red B	(X)
Black MG	(IV)	Azo Blue Salt MG and BD (Blue B and BB)	
Black IG	AS–SR+(V)	Red RL	(XI)

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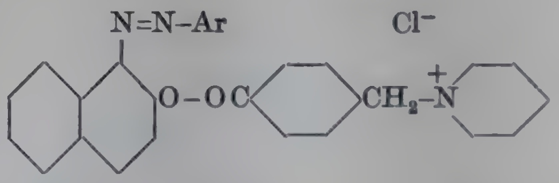
[90] According to *BIOS* Misc. 20, the 5-methoxy derivative of Naphtol AS-L4G is used.

Four Rapidazols are included in the IG range of azoic printing colors, and their composition is as follows :

Rapidazol	*Naphtol*	*Diazo component*
Blue IB	AS	Variamine Blue B
Navy Blue G	AS–D	Variamine Blue B
Navy Blue RR	AS–D	Variamine Blue RT
Black B	AS–OL	Variamine Blue B

The Neocotones (Cb) (Neogenoles, S; Tinogenales, Gy) represent a new type of azoic printing color.[91] The pigment is converted into a water-soluble product by the introduction of a group which splits off under alkaline conditions, regenerating the original pigment. Neocotone dyes may be printed alongside vat dyes. In the recommended procedure for the application of the Neocotones, the fabric is printed with a neutral color paste, steamed (neutral) for 7–15 minutes, and then led in open width through a cold bath containing caustic soda, barium chloride and potassium chloride; washed, soured with dilute hydrochloric acid at 70–80°, washed and soaped.[92] The insoluble azo pigments are first prepared in substance and then acylated with agents containing solubilizing groups; e.g., 1-arylazo-2-naphthol is acylated with *p*-chlormethylbenzoyl chloride in pyridine to form a quaternary ammonium salt (I).[93] Azoic dyestuffs may also be solubilized by means of various other acylating agents such as 3-sulfo- and 3,5-disulfobenzoyl chloride in pyridine solution. It has been suggested that when the azoic pigment is derived from BON acid arylamides, two acyl residues are introduced; one acyl group attaches itself to the hydroxyl and the other to the NH group (cf. the action of cyanuric chloride, mentioned earlier). The Neocotones have not attained technical success and are little used in printing practice, since there are difficulties in their application and they offer no real advantage over the Rapidogen type of azoic printing color. Ufimtsev has described methods for the production of water-soluble pyridinium salts of the esters of azoic dyes, using chloroacetyl chloride and pyridine, or the chloride of nicotinic acid and methyl iodide.[94] Diazotized sulfamic acids (e.g., II from Variamine Blue) couple with " naphthols " to



(I)

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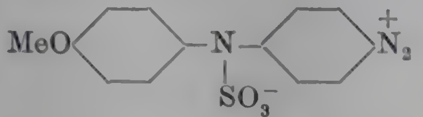
[91] Ciba, USP 2,095,600; BP 480,358; 482,184; 512,664.

[92] Graenacher and Reichart, *Melliand Textilber.* **20**, 288 (1939).

[93] Graenacher, Ackermann, Bruengger and Ciba, USP 2,235,480.

[94] *J. Applied Chem.* (*USSR*) **14**, 600 (1941).

give water-soluble dyes which can be applied to cotton, wool or silk in neutral or slightly acid medium by padding or printing. Treatment with dilute sulfuric acid at 50–100° for a few seconds produces the insoluble azoic dye.[95]


(II)

A method of converting azoic dyes containing anthraquinone residues into a soluble derivative, from which the pigment can be regenerated on the fiber, is mentioned in Chapter XXXIV.

IDENTIFICATION OF AZOIC DYES

In view of the technical importance of the azoic coloring matters, methods for their identification are of interest.[96] The general procedure is to reduce the pigment and identify the products.[97] The azoic dye may be stripped from the fiber by means of a solvent such as pyridine or by destroying the cellulose with concentrated sulfuric acid and recovering the pigment by dilution with water. Ethylenediamine is a useful solvent for azoic pigments; for reduction, they may be dissolved in 60–70% ethylenediamine and hydrosulfite added to the hot solution.[98] Aqueous dioxane is another useful solvent for the hydrosulfite reduction; on careful dilution of the dioxane with water, the 1-amino derivative of the " naphthol " separates, and from the filtrate the diazonium component can be isolated as the benzoyl derivative of the amine by benzoylation without isolation of the amine.[99]

During reductive fission a nitro group in an azoic pigment is simultaneously reduced to the amino group. With *o*-nitroazo compounds, the *o*-diamines may be isolated and characterized as the quinoxalines; with *p*-nitroazo compounds care must be exercised to isolate the oxidizable *p*-diamines in pure form.

Azoic dyes may be identified by fission with fuming nitric acid; the method is particularly useful if the pigment contains a nitro group.[100] The products of the fission are a diazonium nitrate, identified by coupling with β-naphthol, and a nitro derivative of the "naphthol" component. If the diazonium component does not contain a nitro group, it is nitrated by the fuming nitric acid treatment; the nitro group is *para* to the diazonium group if this position is unoccupied, and *ortho* if the *para* is occupied. Azoic dyes derived from the same diazonium salt give color reactions with certain reagents (e.g., concentrated sulfuric acid; pyridine + 4% caustic soda solution; hot strong caustic soda solution, followed by sodium sulfide; boric acid in sulfuric acid; nitric acid added to sulfuric acid solution), which are characteristic of the diazonium component and largely independent of the "naphthol" component. Crystallization characteristics and absorption spectra may then be used for identifying both the components.[101]

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[95] Lantz, *Teintex.* **13,** 191 (1948); USP 2,500,080.

[96] Cf. Rowe, *J. Oil & Colour Chemists' Assoc.* **21,** 189 (1938).

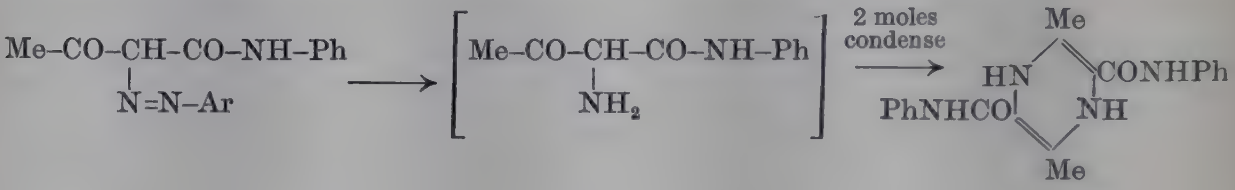
[97] See however Vesce, Microscopic Identification of Azo Dyes and Organic Pigments, Harman Color and Chemical Co., New Jersey; and Vesce *in* Mattiello's Protective and Decorative Coatings, Vol. II, Wiley, New York, 1942, p. 124. Azoic and other pigments and lakes are identified by microcrystallization from conc. sulfuric acid and observation of the crystals under the microscope.

[98] Clayton, *J. Soc. Dyers Colourists* **53,** 178 (1937).

[99] Koch and Milligan, *Anal. Chem.* **19,** 312 (1947); see also Koch, Milligan and Zuckerman, *Ind. Eng. Chem. Anal. Ed.* **16,** 755 (1944).

[100] Burr and Rowe, *J. Soc. Dyers Colourists* **44,** 205 (1928).

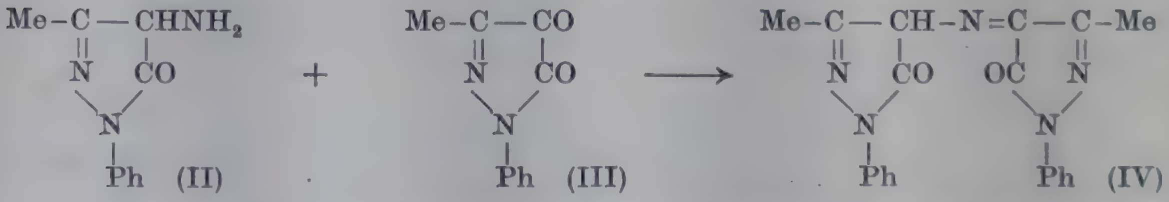
Azo and azoic dyes from acetoacetic arylides do not give the corresponding aminoketones on reduction, but dihydropyrazines (I).[102] Burr



(I)

and Rowe have identified the Hansa Yellow type of pigment by their general properties as derivatives of acetoacetarylides and by the action of fuming nitric acid; the diazonium nitrate of the first component is formed (although the yield is very low), and is identified by coupling with β-naphthol.

The pyrazolones are not used in azoic dyeing, but they are valuable as coupling components for the preparation of yellow and orange pigments. Such azoic pigments (as well as azo dyes) do not yield the corresponding 4-aminopyrazolone on reduction. This is first formed, but undergoes



further changes. With 1-phenyl-3-methyl-5-pyrazolone for instance, the amine (II) oxidizes to the α-diketone (III); (II) and (III) then react with each other to form the red rubazonic acid (IV).

RECENT TRENDS

The possibilities for azoic combinations being unlimited, patents still appear on the preparation of new "naphthols" and bases in spite of the plethora of patents on the subject during the quarter century preceding the war. It is noticeable, however, that the major activity is in new and improved methods of stabilizing diazonium salts, and there are more attempts at modifying the properties of azoic dyes by introducing new diazonium components rather than new "naphthols." An interesting example of a simple modification in the usual Naphtol AS type is the condensation product of BON acid and 2-aminohydroquinone 1-ethyl 4-methyl ether, which is claimed to yield a fast brown in combination with Fast Scarlet Salt GG.[102a]

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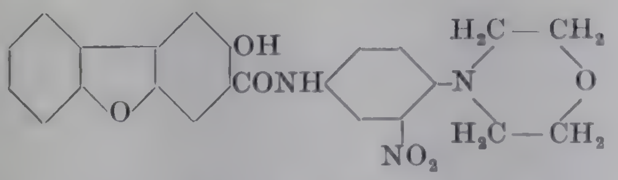
[101] Cf. *BIOS* **763**.

[102] Fierz-David, *J. Soc. Dyers Colourists* **45**, 133 (1929).

Increase in molecular weight by increasing the complexity of the fused ring systems in *o*-hydroxycarboxylic acid arylides leads to greater substantivity, and also has a bathochromic effect. The modification of the naphthol may be in the acid or amine half; thus BON acid may be replaced by analogs of anthracene, carbazole and benzocarbazole; and aniline in Naphtol AS by amines derived from naphthalene, anthracene, carbazole, pyrene and chrysene.[103] The condensation of BON acid with aminopyrenes and aminochrysenes gives "naphthols" useful for brown, corinth and black shades.[103] The arylides of 3-hydroxyfluorene-2-carboxylic acid have greater substantivity than the 2,3-isomers, and are useful for olive, khaki and brown shades.[104] The condensation products of 2,7-diaminofluorene with BON acid and with acetoacetic ester are claimed to excel the present members of the Naphtol AS series in substantivity and in the fastness of the azoic shades.[105] Highly substantive "naphthols" are obtained by condensing BON acid with a 2-amino-3-alkoxydiphenyleneoxide, substituted in the 6- or 7-position by chlorine, methyl or methoxyl (cf. Naphtol AS–S).[106] The introduction of the morpholine nucleus into "naphthols" has been recently suggested.[107] *p*-Nitrochlorobenzene or 2,4-dinitrochlorobenzene is condensed with morpholine, and the *p*-nitro group is reduced.



(I)

The amine is then condensed with BON acid or other *o*-hydroxycarboxylic acid. An example of a "naphthol" of this type is (I). High substantivity to cotton is claimed for the arylamides from aminoarylpyridines condensed with BON and similar acids.[108] Other examples of heterocyclic amines condensed with BON acid are 2-amino-6-ethoxybenzothiazole[109] and aminoazaphenanthrenes.[110]

[102a] Ciba, BP 634, 390. [103] Cf. Ciba, BP 515,381. [104] IG, BP 494,423.

[105] Poraî-Koshits and Perekalin, *Org. Chem. Ind.* (*USSR*) **4**, 165 (1937).

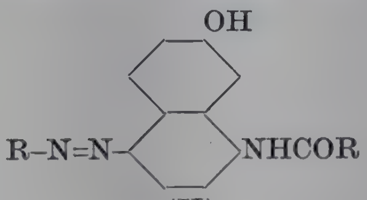
[106] IG, DRP 718,348.

[107] Grimmel, Guenther and General Aniline and Film, USP 2,408,421: 2,419,932: BP 613,130.

[108] Heilbron, Haworth, Hey and ICI, BP 518,886; Kershaw, Kenneth, Saunders and ICI, BP 519,437.

Few compounds, other than the arylides of *o*-hydroxycarboxylic acids and of β-ketonic acids, have been suggested as azoic coupling components. " Resistant black shades " are obtained by using 3-amino-4-(2′-)naphthalene-azo-2-naphthol as a " naphthol " and coupling with diazonium salts such as 4′-nitro-1-amino-2,5-dimethoxyazobenzene.[111] Other examples are (II);[112] di- or triarylmethanes having one or more hydroxyl groups and a free coupling position;[113] 2-hydroxy-2′-aryl-ψ-naphthazimides; and hydroxy-benz(α)acridines.[114]

In view of the very small number of yellow-producing " naphthols " commercially available, attempts are being made to extend the range and to arrive at β-ketocarboxylic acid arylides with improved properties. The substantivity of acylacetarylides may be increased by the introduction of heterocyclic rings, and there are many patents relating to derivatives of 2-indolylacetic esters,[115] 2-amino-3,6-dimethoxydibenzofuran,[116] amino-2-phenylbenzoxazoles and -phenylbenzothiazoles,[117] and 5-amino-2-phenyl-ψ-azimidobenzene.[118] The bis-acylacetamido derivatives of trinuclear compounds (III), in which X = a bivalent radical, represent a general type yielding yellow to orange shades with good fastness properties.[119] The " naphthol " (IIIa) has affinity for cellulose and the yellow azoic shades are fast to light.[119a]



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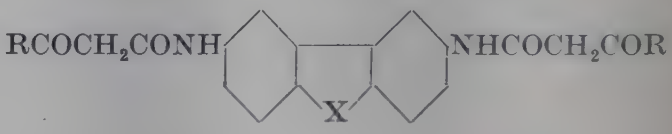

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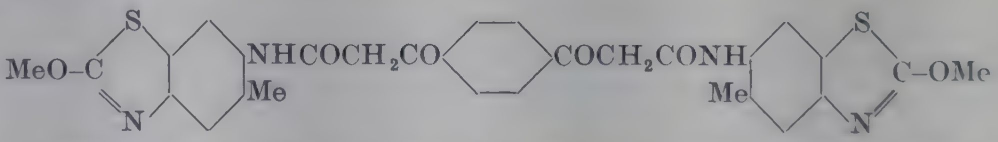

(IIIa)

In " naphthols " of the AS–G type the replacement of benzidine by numerous other diamines (e.g., thioaniline, diaminodiphenyl ether, aminobenzoyl-*p*-phenylenediamine, and diaminobenzophenone) has been suggested.[120]

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[109] Ciba, BP 578,268.

[110] IG, BP 451,932; 461,425. See also Orem *et al.* USP 2,465,979; 2,468,457.

[111] Ciba, SP 215,051–8.

[112] du Pont, BP 499,335–6.

[113] Burawoy, Barclay and Thomson, BP 561,302.

[114] Ciba, BP 516,585; Trepagnier and du Pont, USP 2,373,926; 2,499,800.

[115] IG, BP 512,799.

[116] Ciba, BP 540,743.

[117] Kuhlmann, BP 516,851.

[118] Ciba, BP 498,051.

[119] Dahlen, Zwilgmeyer and du Pont, USP 2,059,852.

[119a] Francolor, BP 598,985.

[120] Zitscher and Schmitt, USP 1,580,709; 1,594,864; 1,634,090.

Acylacetarylamides which do not have adequate substantivity for application in dyeing may be useful in printing compositions for yellow prints, if the fastness is good. Examples have been quoted in the Rapid Fast and Rapidogen colors, and other examples are 3-chloro-4-ethoxyacetoacetanilide and 4-cyano-2,5-dialkoxyacetoacetanilides.[121] The disadvantage of dual coupling positions in the AS–G type of component may be obviated by using the condensation product of a monoacylated benzidine with acetoacetic ester. Such compounds (e.g., 4-acetamido-4′-acetoacetamido-3,3′-dimethyldiphenyl) are suitable for printing.[122]

While second components with reactive methylene groups are generally regarded as suitable for yellows, aminoazo compounds from diazotized alkoxyanilines and 2,5-bis-β-hydroxyethylaniline give fast red shades by coupling with acylacetarylamides;[123] and diazotized Safranines couple with acetoacetarylides to blue and green shades.[124]

By using substantive diazonium salts the ordinary azoic dyeing process may be reversed. The amines used must have at least one of the following characteristics: (a) a group of 3 or more 5- or 6-membered aromatic or heterocyclic rings connected so that the molecule contains a continuous chain of conjugated double bonds; (b) the group –HN–CO–NH–, or a cyanuric ring; or (c) the group Ar–N=N–Ar′ or Ar–CH=CH–Ar′. Further, they must contain at least one nitrogen in a 6-membered ring, quaternary nitrogen, or a polyglycol ether radical.[125] Thus cotton is dyed yellow and orange respectively by treatment with a cold solution of diazotized 3-amino-7,8-benzacridine or aminobenzophenazine, and developing with 1-phenyl-3-methyl-5-pyrazolone. Similarly, cotton grounded with the diazonium salt of 9,10-(4′-aminophenylthiazolo)-4-azaphenanthrene (IV) gives red shades with β-naphthol and Naphtol AS, and yellow shades with diacetoacet-*o*-tolidide.

Among the new amines suggested as Fast Bases for azoic dyeing may be mentioned 3-chloro-1-aminoanthraquinone which is stated to yield shades which are "exceptionally brilliant" and to have "extraordinary light fastness";[126] a series of sulfones (cf. Fast Scarlet LG Base and Fast Red GTR Base);[127] aryl esters of orthanilic acid for bright orange shades of good fastness to light;[128] amines containing a keto group in addition to alkoxy groups, e.g., 3-amino-2,5-dimethoxyacetophenone which gives azoic shades fast to peroxide;[129] amines (e.g., V) containing a sulfon-n-butylamide group for bright reds of high all-round fastness[130] (cf. Fast Red ITR Base); amines containing a sulfonyl fluoride group for bright and wash-fast shades;[131] amines containing two sulfonamido groups (e.g., VI);[132] chloroalkyl ethers of aminodiphenylamines for shades of superior fastness and brightness;[133] diaminodiphenyldisulfides such as (VII) for shades fast to alkali boil;[134] aminoindazoles for corinth shades;[135] Blue Base BB analogs in which the benzoyl group is replaced by furoyl[136] or by picolinyl, nicotinyl and similar acyl groups;[137] *N*,*N*-diphenyl-*N′*-(2,5-diethoxy-4-amino)phenylurea for blue shades;[138] 2,7-diaminophenanthraquinone for blue to blue-black shades;[139] 5-*N*-(*p*-amino)phenylamino-1,3-benzodioxole (VIII) for blue shades;[140] 6-*N*-(*p*-amino)phenylamino-1,3-benzodioxane (IX) for violet shades; 6-*N*-(*p*-amino)phenylamino-1,4-benzodioxane for strong blue to violet shades;[141] 1-arylazo-2-naphthols such as (X) containing an amino

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[121] ICI, BP 516,689–90; Glahn and Bergstrom, USP 2,453,692.

[122] Dahlen, Bigelow, Zwilgmeyer and du Pont, USP 2,193,553.

[123] Saunders and ICI, BP 513,323.

[124] IG, BP 492,290. See also Francolor, BP 632,595.

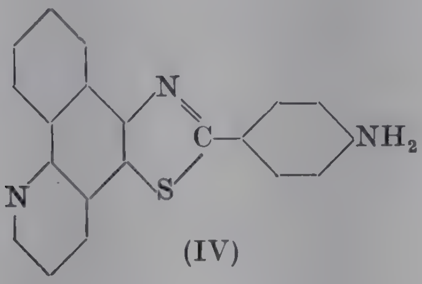
[125] IG, BP 489,429.

[126] *FIAT* **1313** III.

[127] Manchester Oxide Co., Clayton and Bann, BP 546,301; 546,428; 546,277–81.

[128] Kuhlmann, BP 497,862.

[129] IG, BP 516,773.



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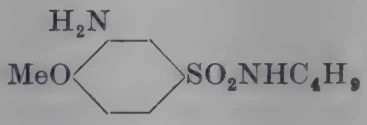

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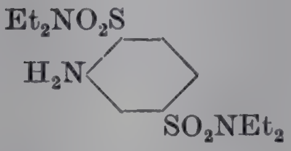

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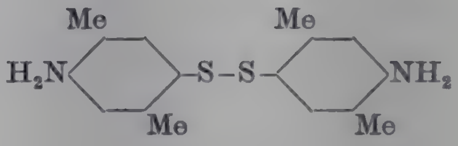

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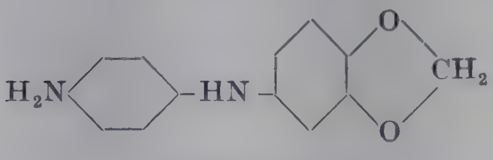

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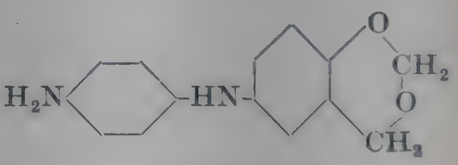

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[130] IG, BP 498,534.

[131] Lecher, Parker, Hofmann and American Cyanamid, USP 2,427,995; 2,436,697.

[132] Kuhlmann, BP 518,791.

[133] Goulding, Parker, Denton and American Cyanamid, USP 2,426,576.

[134] Manchester Oxide Co. *et al.*, BP 559,784.

[135] Francolor, BP 599,834.

[136] Markush and Pharma-Chemical Corp., USP 2,074,186.

[137] Gross and du Pont, USP 2,439,728.

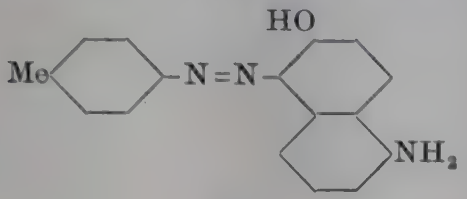
[138] Ciba, SP 217,227; see also 220,403.

[139] Nikoliuk, *Prom. Org. Khim.* **6**, 581 (1939).

[140] Lecher, Goulding and American Cyanamid, USP 2,409,133.

[141] American Cyanamid, USP 2,409,134; Conn, Adams and Goulding, USP 2,419,334. See also USP 2,501,188.

group in the other ring so that it is readily diazotizable,[142] tetraminophthalocyanines for green and greenish blue shades of good fastness;[143] and



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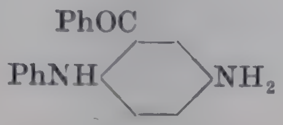

(XI)

aminodiphenylamines (e.g., XI) containing a *C*-benzoyl group for deep, fast blacks.[144]

PIGMENTS

Azoic dyes[145, 146] include pigments prepared in substance for the coloration of nontextile materials such as paints, varnishes, lacquers, printing inks and plastics. A recent development is the use of pigments for textiles, as in the mass pigmentation of viscose and in pigment printing. Several azoic pigments are identical with azoic dyes produced on the fiber; but usually the two types of azoics are distinct, since the nature of the azoic dyeing process circumscribes the choice of the two components, especially the "naphthol." The fastness requirements are different in the two cases; and in general less expensive components must be employed in the preparation of pigments for nontextile purposes. β-Naphthol is used as the second component much more frequently than the Naphtol AS type. Components such as acetoacetanilide (I) and its derivatives, especially the *m*-xylidide (II), 1-phenyl-3-methyl-5-pyrazolone (III), and 2,4-dihydroxyquinoline, which are not employed in azoic dyeing, are used for the preparation of yellow pigments in substance. The physical state or particle size of a pigment color is important and this is not merely a matter of suitable grinding before use. The conditions of coupling, filtration and drying have to be carefully controlled, since these affect the color of the pigment, as well as its dispersibility in oil. Certain pigments, such as 2,4-dinitrobenzeneazo-β-naphthol, must not be used with red lead or orange lead, since such dry mixtures are very inflammable owing to the presence of the nitro groups, and grinding them in a ball mill might cause an explosion.[145]

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[142] Zwilgmeyer and du Pont, USP 2,193,996–8.

[143] Blackshaw, Haddock and ICI, BP 535,935.

[144] IG, BP 512,844.

[145] For an account of the color, constitution, properties and identification of the insoluble azo coloring matters, see ref. 96; and Yates, *Industrial Chemist* **18,** 107, 215 (1942).

[146] For their use in paints and the determination of their fastness properties, see Walker, *J. Oil & Colour Chemists' Assoc.* **30,** 91 (1947). For a general account of organic pigments, see Mattiello, Protective and Decorative Coatings, Vol. II, Wiley, New York, 1942.

Table VIII gives the constitution of the IG range of azoic pigments.[147] Corresponding to the Lithol, Hansa and Permanent colors (IG), other manufacturers make similar pigments under their own trade names, e.g., Monolite (ICI). The Vulcan pigments (IG) are recommended as rubber colors.

TABLE VIII

AZOIC PIGMENTS

Pigment	*Diazo component (Fast Base)*	*Coupling component*
Hansa Yellow A Supra; KG	Red G, GL	(I)+(II)
Hansa Yellow G; GA; GT	Red G, GL	(I)
Hansa Yellow GGR	99% Red G, GL+ 1% Bordeaux GP	(I)
Hansa Yellow 3G	4-Chloro-2-nitroaniline	(I)
Hansa Yellow 5G	Orange GR 80%+ Red G, GL 20%	(I)
Hansa Yellow 10G (10GT paste)	4-Chloro-2-nitroaniline	*o*-Chloro-(I)
Hansa Yellow GE	4-Chloro-2-nitroaniline 99% +Bordeaux GP 1%	(I)
HansaYellow GR	4-Chloro-2-nitroaniline	(II)
Hansa Yellow R	Scarlet GG	(III)
Hansa Yellow 3R	Bordeaux GP	*o*-Methyl-(I)
Hansa Yellow RN	Bordeaux GP	*o*-Methoxy-(I)
Permanent Yellow NCG	2,4-Dichloroaniline	Naphtol AS–G
Permanent Yellow 5899	Red TR	Naphtol AS–G
Permanent Yellow NCR	Orange GR	2,4-Dihydroxyquinoline
Lithol Fast Yellow R		
Permanent Yellow R	Yellow G, GC	*p*-Nitro-(III)
Permanent Yellow 4R	Yellow G, GC	(III)
Spinning Yellow GGV	Red TR	4-Chloro-2,5-dimethoxy-(I)
Spinning Yellow RA	4,4′-Dichloro-2-amino-5-methyldiphenyl ether	Naphtol AS-G
Vulcan Fast Yellow G	3,3′-Dichlorobenzidine	Methyl-(I)
Vulcan Fast Yellow 5G	3,3′-Dichloro-5,5′-dimethoxybenzidine	(II)
Vulcan Fast Yellow GR	3,3′-Dichlorobenzidine	(II)
Vulcan Fast Yellow R	*o*-Tolidine	(II)
Permanent Gold Yellow G	Red KB	Naphtol AS–G
Sudan G	Aniline	Resorcinol
Lithol Fast Orange RN	2,4-Dinitroaniline	β-Naphthol
Lithol Fast Orange 3GL 20% paste	3-Nitro-4-amino-1-benzotrifluoride	β-Naphthol
Permanent Orange G	3,3′-Dichlorobenzidine	(III)
Permanent Orange GTR	Orange G, GC 98%+ Aniline 2%	Naphtol AS
Autol Orange	2-Chloro-*p*-toluidine	β-Naphthol

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[147] *BIOS 961*; Report 19, Textile Series, Office of the Quartermaster General, U.S. Dept. of Commerce.

TABLE VIII (*continued*)

Pigment	*Diazo component (Fast Base)*	*Coupling component*
Spinning Orange GA	3-Bromo-1-aminoanthraquinone	2,5-Dimethoxy-(I)
Tuskalin Orange GN	3-Chloro-6-nitroaniline	β-Naphthol
Pigment Orange R	Scarlet G	β-Naphthol
Sudan I	Aniline	β-Naphthol
Vulcan Fast Orange GG	Blue B	(II)
Spinning Orange 4RN	Orange GC	Naphtol AS-OL
Permanent Scarlet R	3-Aminobenz-*n*-butylamide	*p*-Toluidide of BON acid
Lithol Fast Scarlet GRN, R, RB, RN; Hansa Red B	Red G, GL	β-Naphthol
Vulcan Fast Rose G	4-Methyl-3-amino-benzoyl-*m*-xylidide	Naphtol AS–E
Autol Red RLP	α-Naphthylamine	β-Naphthol
Flag Red Pigment; Permanent Red FFR	Scarlet GG	Naphtol AS
Permanent Red FRLL	Scarlet GG	Naphtol AS–OL
Helio Fast Red RBR	*m*-4-Xylidine	β-Naphthol
Lithol Fast Red Toner B	3-Amino-4-methoxydiphenylsulfone	*o*-Xylidide of BON acid
Lithol Fast Red Toner R	Scarlet LG	*m*-Xylidide of BON acid
Tuskalin Red B	Red B	β-Naphthol
Para Red; Pigment Red B, RN	Red GG	β-Naphthol
Permanent Red FR	Yellow G, GC	Naphtol AS
Permanent Red F2R	Aniline	Naphtol AS
Permanent Red F4R	Scarlet G	Naphtol AS–E
Permanent Red F4RH	Red TR	Naphtol AS–TR
Permanent Red FFR	2,5-Dichloroaniline	Naphtol AS
Permanent Red FRL	2,5-Dichloroaniline	*p*-Toluidide of BON acid
Permanent Red GG	2,4-Dinitroaniline	β-Naphthol
Permanent Red L, FGR	Trichloroaniline	Naphtol AS–D
Permanent Red R	2-Chloro-4-nitroaniline	β-Naphthol
Helio Red RBL	Red G, GL	β-Naphthol
Permanent Red 4R		
Permanent Red 4RT	Red TR	Naphtol AS–TR
Sudan II	*m*-4-Xylidine	β-Naphthol
Sudan IV	Garnet GBC	β-Naphthol
Autol Red GL	Red R	β-Naphthol
Vulcan Fast Red B	3,3′-Dichlorobenzidine	1-Phenyl-5-pyrazolone-3-carboxylic ethyl ester
Vulcan Fast Red GF	Red BB	*p*-Methyl-(III)
Oil Vermilion	Red BB	β-Naphthol
Pigment Purple		
Pigment Rubine FBH	Red KB	4-Chloro-*o*-toluidide of BON acid
Vulcan Fast Rubine B	3-Amino-4-methoxybenzanilide	Naphtol AS
Permanent Carmine FB	Red ITR	Condensation product of Red Base ITR and BON acid

TABLE VIII (*continued*)

Pigment	*Diazo component (Fast Base)*	*Coupling component*
Permanent Carmine FB extra powder	Red ITR	Naphtol AS–ITR
Bordeaux Pigment	Bordeaux GP	Naphtol AS–D
Permanent Bordeaux F3R	Red B	Naphtol AS–BO
Permanent Bordeaux FRR	Red RL	Naphtol AS–D
Vulcan Fast Bordeaux B	3-Amino-4-methoxybenzanilide	Naphtol AS–BS
Permanent Violet FR	2-Nitro-*p*-anisidine	Naphtol AS–BO
Blue 4022	Blue B	Naphtol AS–BO
Dianisidine Blue	Blue B	β-Naphthol
Spinning Khaki GV	Orange G, GC	Naphtol AS–LB
Brown Pigment L 878	*o*-Anisidine-4-sulfondibutylamide	Naphtol AS–LB
Permanent Brown B	Red TR	Naphtol AS–BT
Permanent Brown FG	Scarlet GG	Naphtol AS–BG
Spinning Brown RA	*p*-Toluidine	Naphtol AS–LB
Spinning Brown 5RV	3-Amino-4-methoxybenzanilide	Naphtol AS–LB

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